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N. Y. C.

QUALITATIVE CHEMICAL ANALYSIS

A GUIDE IN QUALITATIVE WORK, WITH DATA FOR ANALYTICAL OPERATIONS AND LABORATORY METHODS

BY

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SEVENTH EDITION, THOROUGHLY REVISED

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PREFACE TO THE SEVENTH EDITION.

Since the last revision of this very comprehensive text on Qualitative Analysis was issued, a considerable number of new methods of analysis have been published, and some of these have been found to be valuable and have come into more or less general use.

Many of the new methods have been tried out and some have been found to be unreliable unless extreme care is taken or only pure solutions used. The attempt has been made to include in this revision only those methods which have been found to be reliable.

A very marked change has also taken place in the method of presentation of chemical reactions. Ionic reactions are given in many texts to the exclusion of molecular reactions. Physical chemical theories are also frequently presented and discussed at great length.

The attempt has been made in the revision of this text to present only briefly the modern conceptions of solution, leaving a fuller presentation for the lecturer or separate texts on Physical Chemistry. Molecular reactions have also been largely retained in the belief that the material to be analyzed by the chemist in practical work is quite as often a molecular compound as an ion.

All molecular weights, solubilities and other constants of the elements and their principal compounds have been brought up to date. The principal minerals, methods of preparation and determinations of elements, as well as the reactions, have been revised, references being given to the literature as heretofore.

In general, the attempt has been made to retain the excellent features of this text which have given it such an extended use in the past, both as a class room and as a reference text, while adding the valuable results of recent progress in the science.

Acknowledgment is made with pleasure of valuable assistance rendered the undersigned in preparing the revision to Professor R. J.

Colony of Cooper Union, who revised the sections on the properties, occurrence and preparation of the metals; to Mr. Wm. H. Ulrich, who tried out many of the new methods; to Mr. N. F. Borg, who contributed much of the revision of the acids; and to Mr. M. P. Matthias, who has revised the Index.

J. C. OLSEN

October 2, 1916.

PREFACE TO THE FIRST EDITION.

In this, the fifth full revision of this manual, the text has been rewritten and the order of statement in good part recast. The subject-matter is enlarged by fully one-half, though but one hundred pages have been added to the book.

It has been our aim to bring the varied resources of analysis within reach, placing in order before the worker the leading characteristics of elements, upon the relations of which every scheme of separation depends. This is desired for the working chemist, and no less for the working student. However limited may be the range of his work, we would not contract his view to a single routine. It is while in the course of qualitative analysis especially that the student is forming his personal acquaintance with the facts of chemical change, and it is not well that his outlook should be cut off by narrow routine at this time.

The introductory pages upon Operations of Analysis, setting forth some of the foundations of qualitative chemistry, consist of matter restored and revised from the editions of 1874 and 1880. This subject-matter, omitted in 1888, is now desired by teachers. For the portion upon Solution and Ionization, we are indebted to Dr. Eugene C. Sullivan, a pupil of Professor Ostwald, now teaching qualitative analysis. The pages upon the Periodic System have been added to afford a more connected comparison of the elements than that undertaken in each group by itself, in previous editions, and referred to in the preface in 1874. The use of notation with negative bonds, in balancing equations for changes of oxidation, introduced by one of the authors in 1880, has been retained substantially as in the last edition. Other authors adopt the same notation with various modifications. For the present revision there has been a general search of literature, and authorities are given for what is less commonly known or more deserving of further

inquiry. The number of citations is so large that to save room special abbreviation is resorted to.

For convenient reference, on the part of teachers, students and analysts using the book, the section for each element and each acid is arranged in uniform divisions. For instance, in each section, solubilities are given in paragraph 5, the action of alkalis in paragraph 6*a*, the action of sulphur compounds in paragraph 6*e*, etc. In the paragraph (9) for estimation it should be said, nothing more than a general statement of methods is given, for the benefit of qualitative study, without directions and specifications for quantitative work, in which, of course, other books must be used.

The authors desire to say with the fullest appreciation that Perry F. Trowbridge, instructor in Organic Chemistry in this University, has performed a large amount of labor in this revision, collecting data from original authorities, confirming their conclusions by his own experiments, elaborating material, and making researches upon questions as they have arisen.

University of Michigan,
April, 1901.

CONTENTS.

PART I.—THE PRINCIPLES OF ANALYTICAL CHEMISTRY.

PAGE

The Chemical Elements and their Atomic Weights 1
Table of the Periodic System of the Chemical Elements 2
Discussion of the Periodic System 3
Classification of the Metals as Bases 10
Commonly Occurring Acids 13
The Operations of Analysis 13
Solution and Ionization 20
Order of Laboratory Study 25

PART II.—THE METALS.

THE SILVER AND TIN AND COPPER GROUPS.

(FIRST AND SECOND GROUPS).

General Discussion 27

THE SILVER GROUP (FIRST GROUP).

Lead 29
Mercury 37
Silver 45
Comparison of Certain Reactions of the Metals of the Silver Group 51
Table for Analysis of the Silver or First Group 52
Directions for Analysis with Notes 53

THE TIN AND COPPER GROUP (SECOND GROUP).

THE TIN GROUP, OR SECOND GROUP, DIVISION A.

Arsenic 56
Antimony 72
Tin 82
Comparison of Certain Reactions of Arsenic, Antimony and Tin 90
Gold 91
Platinum 93
Molybdenum 97

THE COPPER GROUP, OR GROUP II, DIVISION B.

Bismuth 100
Copper 104
Cadmium 110
Comparison of Certain Reactions of Bismuth, Copper and Cadmium 113

PAGE

The Precipitation of the Metals of the Second Group 113
Table for the Analysis of the Tin Group (Second Group, Division A). 116
Directions for Analysis with Notes 118
Table for Analysis of the Copper Group (Second Group, Division B).. 126
Directions for Analysis with Notes 125

RARER METALS OF THE TIN AND COPPER GROUP.

Ruthenium 131
Rhodium 132
Palladium 133
Iridium 134
Osmium 135
Tungsten 136
Germanium 137
Tellurium 138
Selenium 139

THE IRON AND ZINC GROUPS (Third and Fourth Groups) 141

THE IRON GROUP (THIRD GROUP).

Aluminum 144
Chromium 148
Iron 153
Table for Analysis of the Iron Group (Third Group) 163
Directions for Analysis with Notes 164

THE ZINC GROUP (FOURTH GROUP).

Cobalt 167
Nickel 173
Manganese 177
Zinc 183
Comparison of Some Reactions of the Iron and Zinc Group Bases 187
Table for the Analysis of the Zinc Group (Fourth Group)..... 188
Directions for Analysis with Notes 189
Analysis of Iron and Zinc Groups after Precipitation by Ammonium Sulphide 191
Iron and Zinc Groups in Presence of Phosphates..... 193
Iron and Zinc Groups in Presence of Oxalates..... 194
Table of Separation of Iron, Zinc and Calcium Group Metals and Phosphoric Acid by Means of Alkali Acetate and Ferric Chloride 196
Table of Separation of Iron, Zinc and Calcium Group Metals and Phosphoric Acid by Means of Ferric Chloride and Barium Carbonate 197

THE RARER METALS OF THE IRON AND ZINC GROUPS.

Cerium 198
Columbium (Niobium) 198
Didymium 199
Erbium 200
Gallium 200

PAGE

Glucinum (Beryllium) 200
Indium 201
Lanthanum 202
Neodymium 202
Praseodymium 202
Samarium 202
Scandium 202
Tantalum 203
Terbium 203
Thallium 204
Thorium 204
Titanium 205
Uranium 206
Vanadium 207
Ytterbium 208
Yttrium 208
Zirconium 209

THE CALCIUM GROUP (FIFTH GROUP). (THE ALKALINE EARTH METALS) 209

Barium 211
Strontium 214
Calcium 216
Magnesium 220
TABLE FOR THE ANALYSIS OF THE CALCIUM GROUP (FIFTH GROUP) 223
DIRECTION FOR ANALYSIS WITH NOTES 224
SEPARATION OF BARIUM, STRONTIUM, AND CALCIUM BY THE USE OF ALCOHOL 226
ALKALINE EARTH METALS AS PHOSPHATES 226
ALKALINE EARTH METALS AS OXALATES 226

THE ALKALI GROUP (SIXTH GROUP) 227

Potassium 228
Sodium 232
Ammonium 235
Caesium 239
Rubidium 240
Lithium 240
DIRECTIONS FOR ANALYSIS WITH NOTES 242

PART III.—THE NON-METALS.

BALANCING OF EQUATIONS 246
Hydrogen 250
Boron 252
Boric Acid 252
Carbon 254
Acetic Acid 256
Citric Acid 258
Tartaric Acid 259
Carbon Monoxide 262
Oxalic Acid 263
Carbon Dioxide (Carbonates) 267

PAGE

Cyanogen 271
Hydrocyanic Acid 271
Hydroferrocyanic Acid 275
Hydroferricyanic Acid 277
Cyanic Acid 279
Thiocyanic Acid 280
Nitrogen 281
Hydrazoic Acid 282
Nitrous Oxide 283
Nitric Oxide 283
Nitrous Acid 284
Nitrogen Peroxide 285
Nitric Acid 285
Oxygen 291
Ozone 293
Hydrogen Peroxide 294
Fluorine 297
Hydrofluoric Acid 298
Fluosilicic Acid 298
Silicon 299
Silicic Acid 299
Phosphorus 301
Phosphine 304
Hypophosphorous Acid 304
Phosphorous Acid 306
Hypophosphoric Acid 307
Phosphoric Acid 308
Sulphur 313
Hydrosulphuric Acid 315
Thiosulphuric Acid 321
Hyposulphurous Acid 323
Dithionic Acid 324
Trithionic Acid 324
Tetrathionic Acid 325
Pentathionic Acid 325
Table of Thionic Acids 326
Sulphurous Acid 327
Sulphuric Acid 331
Persulphuric Acid 336
Chlorine 337
Hydrochloric Acid 341
Hypochlorous Acid 348
Chlorous Acid 349
Chlorine Peroxide 350
Chloric Acid 350
Perchloric Acid 353
Bromine 354
Hydrobromic Acid 357
Hypobromous Acid 360

PAGE

Bromic Acid 360
Iodine 362
Hydriodic Acid 365
Iodic Acid 369
Periodic Acid 372
Comparative Reactions of the Halogen Compounds 373

PART IV.—SYSTEMATIC EXAMINATIONS.

Removal of Organic Substances 374
Preliminary Examination of Solids 375
Conversion of Solids into Liquids 378
Treatment of a Metal or an Alloy 379
Separation of Acids from Bases 381
Table for Preliminary Examination of Solids 382
Behavior of Substances Before the Blow-Pipe 386
Table of the Grouping of the Metals 387
Table for the Separation of the Metals 388
Acids—First Table 390
Acids—Second Table 398
Acids—Third Table 399
Acids—Fourth Table 400
Notes on the Detection of Acids 401
Principles 405
Equations 409
Problems in Synthesis 410
Table of Solubilities 412
Reagents 415

ABBREVIATIONS.

* Indicates continuance to the present time.

A.——	Liebig's Annalen. 1832*
A. Ch.	Annales de Chimie et de Physique. 1789*
Am.	American Chemical Journal. 1879*
Am. S.	American Journal of Science. 1818*
	Analyst. 1876*
Arch. Pharm.	Archives der Pharmacie. 1822*
Am. Chem.	American Chemist. 1870–77.
B.——	Berichte der Deutschen Chemischen Gesellschaft. 1868*
Bl.	Bulletin de la Societe Chimique. 1859*
B. J.	Berzelius Jahresbericht. 1822–51.
Comey.	Comey's Dictionary of Solubilities. 1896.
C. N.	Chemical News. 1860*
Ch. Z.	Chemiker Zeitung. 1877*
C. r.	Comptes Rendus des Seances de l'Académie des Sciences. 1835*
C. C.	Chemisches Centralblatt. 1830*
Dingl.	Dingler's Polytechnische Journal. 1820*
D.	Dammer's Anorganische Chemie. 1892*
Fehling.	Fehling's Handbuch der Chemie. 1871*
Fresenius.	Fresenius: Qualitative Chemical Analysis. Wells' Trans., 1897.
G. O.	Graham-Otto: Lehrbuch der anorganischen Chemie. 1885.
Gazzetta.	Gazzetta chimica italiana. 1871*
Gilb.	Gilbert's Annalen der Physik und Chemie. 1799–1824.
Gmelin-Kraut.	Gmelin-Kraut: Handbuch der anorganischen Chemie. 1877.
J.	Jahresbericht über die Fortschritte der Chemie. 1847*
J. C.	Journal of the Chemical Society. 1849*
J. pr.	Journal für praktische Chemie. 1834*
J. Soc. Ind.	Journal of the Society of Chemical Industry. 1882*
J. Anal.	Journal of Analytical Chemistry. 1887–1893.
J. Am. Soc.	Journal of the American Chemical Society. 1876*
J. Pharm.	Journal de Pharmacie et de Chimie. 1809*
Ladenburg.	Handwörterbuch der Chemie. 1882–1895.
M.	Monatshefte für Chemie. 1880*
	Menschutkin. *Locke's Translation.* 1895.
Phil. Mag.	Philosophical Magazine. 1798*
Pogg.	Poggendorff's Annalen der Physik und Chemie. 1824–1877.
Proc. Roy. Soc.	Proceedings of the Royal Society of London. 1832*
Pharm. J. Trans.	Pharmaceutical Journal and Transactions. 1841*
Ph. C.	Pharmaceutische Centralhalle. 1859*
Tr.	Transactions of the Royal Society. 1665*
Watt's.	Watt's Dictionary of Chemistry. 1888.

W. A.	Wiedemann's Annalen. 1877*
W. A. (Beibl.)	Wiedemann's Annalen Beiblätter. 1877*
Wormley.	Wormley's Microchemistry of Poisons. 1867.
Wurtz.	Dictionnaire de Chimie. 1868.
Z.	Zeitschrift für analytische Chemie. 1862.*
Z. Ch.	Zeitschrift für Chemie. 1865–1871.
Z. anorg.	Zeitschrift für anorganische Chemie. 1891*
Z. angew.	Zeitschrift für angewandte Chemie. 1888*
Z. phys. Ch.	Zeitschrift für physicalische Chemie. 1887*

INTERNATIONAL ATOMIC WEIGHTS FOR 1916

		O = 16
Aluminum	Al	27.1
Antimony	Sb	120.2
Argon	A	39.88
Arsenic	As	74.96
Barium	Ba	137.37
Bismuth	Bi	208.0
Boron	B	11.0
Bromine	Br	79.92
Cadmium	Cd	112.40
Cæsium	Cs	132.81
Calcium	Ca	40.07
Carbon	C	12.00
Cerium	Ce	140.25
Chlorine	Cl	35.46
Chromium	Cr	52.0
Cobalt	Co	58.97
Columbium	Cb	93.5
Copper	Cu	63.57
Dysprosium	Dy	162.5
Erbium	Er	167.7
Europium	Eu	152.0
Fluorine	F	19.0
Gadolinium	Gd	157.3
Gallium	Ga	69.9
Germanium	Ge	72.5
Glucinum	Gl	9.1
Gold	Au	197.2
Helium	He	4.00
Holmium	Ho	163.5
Hydrogen	H	1.008
Indium	In	114.8
Iodine	I	126.92
Iridium	Ir	193.1
Iron	Fe	55.84
Krypton	Kr	82.92
Lanthanum	La	139.0
Lead	Pb	207.20
Lithium	Li	6.94
Lutecium	Lu	175.0
Magnesium	Mg	24.32
Manganese	Mn	54.93
Mercury	Hg	200.6

		O = .16.
Molybdenum	Mo	96.0
Neodymium	Nd	144.3
Neon	Ne	20.2
Nickel	Ni	58.68
Niton (radium emanation)	Nt	222.4
Nitrogen	N	14.01
Osmium	Os	190.9
Oxygen	O	16.00
Palladium	Pd	106.7
Phosphorus	P	31.04
Platinum	Pt	195.2
Potassium	K	39.10
Praseodymium	Pr	140.9
Radium	Ra	226.0
Rhodium	Rh	102.9
Rubidium	Rb	85.45
Ruthenium	Ru	101.7
Samarium	Sa	150.4
Scandium	Sc	44.1
Selenium	Se	79.2
Silicon	Si	28.3
Silver	Ag	107.88
Sodium	Na	23.00
Strontium	Sr	87.63
Sulfur	S	32.06
Tantalum	Ta	181.5
Tellurium	Te	127.5
Terbium	Tb	159.2
Thallium	Tl	204.0
Thorium	Th	232.4
Thulium	Tm	168.5
Tin	Sn	118.7
Titanium	Ti	48.1
Tungsten	W	184.0
Uranium	U	238.2
Vanadium	V	51.0
Xenon	Xe	130.2
Ytterbium (Neoytterbium)	Yb	173.5
Yttrium	Yt	88.7
Zinc	Zn	65.37
Zirconium	Zr	90.6

Compiled by the International Committee on Atomic Weights, consisting of F. W. Clarke, W. Ostwald, T. E. Thorpe, and G. Urbain.

Jour. Am. Chem. Soc., 1915, 37, 2449.

2. THE PERIODIC SYSTEM OF THE ELEMENTS.

Revised by Charles Baskerville.

Series	Group Zero	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII
		RH R_2O	RH_2 RO	RH_3 R_2O_3	RH_4 RO_2	RH_3 R_2O_5	RH_2 RO_3	RH R_2O_7	
1	.....	H = 1.008	.....	.....	.....	.....	.....	.....	.....
2	He = 4.00	Li = 6.94	Gl = 9.1	B = 11.0	C = 12.00	N = 14.01	O = 16.00	F = 19.0	.....
3	Ne = 20.2	Na = 23.00	Mg = 24.32	Al = 27.1	Si = 28.3	P = 31.04	S = 32.06	Cl = 35.46	.....
4	A = 39.88	K = 39.10	Ca = 40.07	Sc = 44.1	Ti = 48.1	V = 51.0	Cr = 52.0	Mn = 54.93	Fe = 55.84 Ni = 58.68 Co = 58.97
5	.....	Cu = 63.57	Zn = 65.37	Ga = 69.9	Ge = 72.5	As = 74.96	Se = 79.2	Br = 79.92	
6	Kr = 82.92	Rb = 85.45	Sr = 87.63	Yt = 88.7	Zr = 90.6	Cb = 93.5	Mo = 96.0	.....	Ru = 101.7 Rh = 102.9 Pd = 106.7
7	.....	Ag = 107.88	Cd = 112.40	In = 114.8	Sn = 118.7	Sb = 120.2	Te = 127.5	I = 126.92	
8	Xe = 130.2	Cs = 132.81	Ba = 137.37	La = 139.0	Ce = 140.25	Pr = 140.9	Nd = 144.3	.....	Sa = 150.4 Eu = 152.0 Gd = 157.3
9	.....	.....	.....	Er = 167.7	Tm = 168.5	Yb = 173.5	.....	.....	.....
10	.....	.....	.....	.....	.....	Ta = 181.5	W = 184.0	.....	Os = 190.9 Ir = 193.1 Pt = 195.2
11	.....	Au = 197.2	Hg = 200.6	Tl = 204.0	Pb = 207.20	Bi = 208.0	.....	.....	.....
12	Nt = 222.4	.....	Ra = 226.0	.....	Th = 232.4	.....	U = 238.2	.....	.....

Rare earth metals not placed: Dy = 162.5; Ho = 163.5; Lu = 175.0; Tb = 159.2.

§3. In the periodic system of the chemical elements certain regular gradations of chemical character are to be studied and held in view, to simplify the multitude of facts observed in analysis. Passing from **Li** 6.94 to **F** 19.0 in the first Series of this system, the elements are successively less and less of the nature to constitute bases and more and more of the nature to form acids, as their atomic weights increase. The acid-forming elements are electro-negative to the elements which form bases.*

But in passing from **F** 19.0 to the next higher atomic weight, **Na** 23.0, we return from the acid extreme to the basal extreme and begin another period, in gradation through the seven Groups. There is a like return from one extreme to the other in the steps between chlorine and potassium

* Bases are the oxygen compounds of the metals. Acids are compounds of elements for the most part not metals. In the chemical union of sodium with chlorine, for example, these two elements differ widely from each other in their various properties. The chlorine is the opposite of the sodium in that very power by virtue of which the one combines with the other in the making of sodium chloride, a distinct product. In the polarity of electrolysis the sodium is the positive element, while the chlorine is the negative element. The power of opposite action exercised by the one element upon the other, in their combination together, is represented by the opposite polarity of the one in relation to the other during electrolysis. Electrolysis is an exercise of the same energy that is otherwise manifested in chemical union or in a chemical change. Strictly speaking, it may be said that it is only in electrical results that a positive or a negative *polarity* appears. But the term positive polarity, applied to sodium because it goes to the negative pole of a battery, is a term which well designates the oppositeness of the chemical action of sodium in its union with chlorine. That is to say, the metals are in general "positive," the not-metals in general "negative," in the relation of the former to the latter, and this relation may be termed one of "polarity," whether it appear in electrolysis, in chemical combination, or in a chemical change.

In chemical combination, the atoms of each element act with a "polarity," *the extent* of which may be expressed in terms of hydrogen equivalence or "valence." The valence of an element, when in combination with another element, may be counted as relatively "positive" or "negative" to the latter. For example, in the compound known as hydrosulphuric acid, the sulphur is negative, the hydrogen positive, in the relation of one to the other, as represented by the diagram,

$$\begin{matrix} \mathbf{H} + - \\ \mathbf{H} + - \end{matrix} \mathbf{S},$$

in which the plus and minus signs of mathematics are used to represent the "positive" and "negative" activities of chemical elements. That is, the sulphur acts with two units of valence, both in negative polarity. In sulphuric acid the sulphur is positive in relation to both the oxygen and the hydroxyl, as indicated in the diagram

$$\begin{matrix} (\mathbf{HO}) - + \\ (\mathbf{HO}) - + \end{matrix} \mathbf{S} \left\{ \begin{matrix} + - \mathbf{O} \\ + - \\ + - \mathbf{O} \\ + - \end{matrix} \right.$$

That is, the sulphur acts with six units of valence, all in positive polarity. In respect to oxidation and reduction, the difference between the action of sulphur in hydrosulphuric acid on the one hand, and in sulphuric acid on the other hand, is a difference equivalent to eight units of valence, the combining extent of eight atoms of hydrogen. This value is in agreement with the factors of oxidizing agents in volumetric analysis.

In the same sense there is a change of "polarity" equivalent to the extent of eight units of valence, in reducing periodic acid to hydriodic acid, in reducing arsenic acid to arsine, or in reducing carbon tetrachloride to methane. That is, in any of the groups from IV. to VII. there is a difference, equivalent to the combining extent of eight hydrogen units, between the negative polarity of the element in its regular combination with hydrogen, such as $\mathbf{NH_3}$, and its positive polarity in its highest combination with oxygen, such as $\mathbf{NO_2(OH)}$.

and in those between bromine and rubidium. This fact of a periodic return in the gradation of the properties of the elements, as their atomic weights ascend, constitutes *a periodic system.* A period is termed a Series. A Group in this system consists of the corresponding members of all the Series, which members are found to agree in valence, so that the number of the groups, from I. to VII. (not in VIII.), expresses the typical valence of the elements as grouped. Further inquiry shows that all the properties of the elements are in relation to their atomic weights, as they appear in the periodic system. But this system is not to be depended upon to give information of the facts; it is rather to be used as a compact simplification of facts found independently, by the student and by the authorities on whom the student must depend. A full account of the Periodic System, as far as it is understood, is left to works on General Chemistry.

§4. The remarkable position of Group VIII., made up of three series, each of three elements near each other in atomic weight, respectively in Series 4, 6, and 10, is in central relation to the entire system. In this group there is something of a return, from negative to positive polarity, from higher to lower valence. Group VIII. lies between Group VII. and Group I., that is to say in this group there is a return from negative to positive nature, and from higher to lower valence. Moreover, the newly discovered elements related to argon, destitute of combining value as they are, appear to constitute a Group 0. The latest results render this position of the argon group of elements so probable that it has been placed in the chart for convenience of study, subject to further conclusions. (W. Ramsay. *Br. Assoc. Adv. Sci.*, 1897, 598-601; *B.* 1898, **31**, 3111. J. L. Howe, *C. N.*, 1899, **80**, 74; 1900, **82**, 15, 52. Ostwald, *Grundr. Allg. Chem.*, 3te Auf., 1899, S. 45.) In comparison with the members of Group VII. those of Group VIII. certainly have a diminished negative polarity, and a lower valence, the latter being easily variable. Some of the particulars are given below under the head, "Metals in Relation to Iron." The most remarkable thing about Group VIII. is the fact that the return to Group I. from Group VIII. is less complete than the return from Group VII. That is to say, the character of copper is divided between Group VIII. and Group I., and the same is true of silver and of gold. This relation to Group VIII. can be traced, in some particulars, to zinc and cadmium and mercury in Group II. For these reasons Series 4 and 5 may be studied as one *long period* of seventeen members, Series 6 and 7 as another long period and Series 10 and 11 as a third and final long period.

§5. It is to be observed that each one of the Groups, from I. to VII., falls in two columns, a column consisting of *the alternate elements in the group.* Thus, **H, Li, K, Rb** and **Cs** make up the first column of Group I. It is among the alternate members of a group that the closer grade-relations of

the elements are found. The gradations represented under one column are distinct from those under the other in the same group. The well known alternate elements of a Group, so far as found clearly graded together in respect to given properties, are to be studied as a *Family* of elements. Again a number of elements next each other in a Series are to be studied together, either by themselves or with an adjoining half-group.

For the studies of analytical chemistry the following are the more strongly marked of the families of the well known elements.

§6. *The Alkali Metals.*—**Li** 6.94, (**Na** 23.0), **K** 39.10, **Rb** 85.45, **Cs** 132.81. The first part and sodium of the second part of Group I. In the gradation of these elements the basal power increases qualitatively with the rise in atomic weight. The hydroxides and nearly all salts of these metals are freely soluble in water, wherein they are unlike the ordinary metals of all the other groups. For the most part, however, these solubilities increase with the atomic weight of the metal, and the carbonate and orthophosphate of lithium are but slightly soluble.

§7. *The Alkaline Earth Metals.*—(**Mg** 24.32), **Ca** 40.07, **Sr** 87.63, **Ba** 137.37. These metals, like those of the alkalis, form stronger bases as they have higher atomic weights. Both in Group I. and in Group II. the member in Series 3 (**Na**, **Mg**), though in the second set of alternate members, agrees in many ways with the next three of the first set of alternates. The hydroxides of these metals are not freely soluble in water but are regularly more soluble as the atomic weight of the metal is higher. The sulphides are freely soluble; the carbonates and orthophosphates quite insoluble. The sulphates have a graded solubility, decreasing as the atomic weight is higher, an order of gradation the reverse of that of the hydroxides and of wider range. That is, at one extreme the magnesium sulphate is freely soluble, at the other barium sulphate is insoluble.

§8. *The Zinc Family.*—**Mg** 24.32, (**Al** 27.1), **Zn** 65.37, **Cd** 112.4, ——, **Hg** 200.6. These metals, save aluminum, belong to the second alternates of Group II., and, like those of the corresponding half of Group I., in their gradation they are in general less strongly basal as they rise in their atomic weights. Aluminum, here drawn in from Group III. second half, has the valence of the third group, and differs from the others in not forming a sulphide. The sulphide of magnesium is soluble, the sulphides of zinc, cadmium and mercury insoluble in water, and these three show this gradation, that the zinc sulphide is the one dissolved by dilute acid, while the mercury sulphide is the one requiring a special strong acid to dissolve it, both these differences being depended upon in analysis. Mercury, separated from cadmium by two removes in the periodic order, is but a distant member of this family.

§9. *Metals in Relation to Iron.*—**Cr** 52.0, **Mn** 54.93, **Fe** 55.84, **Ni** 58.68,

Co 58.97. The atomic weights of these metals lie nearly together. They all belong to one Series, the fourth, representing Groups VI. and VII., and make the first of the instances of three members together in one series in Group VIII. Chromium, being in the first division of its group, could not be expected to grade with sulphur and selenium, nor would manganese be expected to grade with chlorine and bromine, but the disparity is striking in both cases, especially in the comparison of melting points. The valence of both chromium and manganese appears partly exceptional to their positions in the system but the maximum valence of each is regular. That all of these five elements, neighbors to chlorine and bromine, are counted as metals, is not contrary to the periodic order. Group VIII. binds Group I. to Group VII. After **Co** 58.97 follow **Cu** 63.57 and then **Zn** 65.37. Indeed each of "the well-known metals related to iron" is capable of serving as either a base or an acid, by change of valence. These metals are the special subjects of oxidation and reduction. So far they resemble their non-metallic neighbors, the halogens. Of the five, chromium and manganese (nearest the halogens) form the best known acids. Nickel and cobalt, like copper, have a narrower range of valence, a more limited extent of oxidation and reduction, within which they as readily act. These valences, in capacity of combination with other elements, not including the most unusual valences, may be written in symbols as follows:

2-3-6	2-3-4-6-7	2-3-6	2-3	2-3	1-2	2
Cr ,	**Mn** ,	**Fe** ,	**Ni** ,	**Co** ,	**Cu** ,	**Zn**

On reaching zinc, 65.37, in this gradation, the capacity of oxidation and reduction disappears. Sulphides are formed by such of these metals as act with a valence of two (all except chromium), and these sulphides are insoluble in water. In the conditions of precipitation sulphides are not formed with the metal in any valence other than two. Chromium acting as a base with a valence of three, like aluminum whose only valence is three, refuses to unite with sulphur. Trivalent iron in precipitation by sulphides is mainly reduced to ferrous sulphide (**FeS**). In chromates the chromium valence is reduced from six to three by hydrogen sulphide acting in solution. A carbonate is not formed by chromium, this being another agreement with aluminum, and the same is true of trivalent iron.*

§10. *The Metals not Alkalis in Group I., Second Part, and their Relatives in Group VIII.*—**Cu** 63.57, **Ag** 107.88, ——, **Au** 197.2. In gradation these metals are less strongly basal, and more easily reduced from their compounds to the metallic state, as their atomic weights rise. This is in agreement with the gradation among the second set of alternates in Group II., the Zinc Family. It likewise agrees with second part of Group VII., the halogens. These elements of Group I. are to be studied with those of Group VIII., especially with those respectively nearest them in atomic

* These metals form unstable hydrated basic carbonates.

weight: **Cu** 63.57 with **Ni** 58.68 and **Co** 58.97, **Ag** 107.88 with **Pd** 106.7, and **Au** 197.2 with **Pt** 195.2. Those with atomic weights above that of copper rank as "noble metals," from their resistance to oxidation and other qualities, so ranking in higher degree as their atomic weights increase. Their melting points (those of **Pd, Ag, Au, Pt**) rise in the same gradation.

By action of ammonium hydroxide upon solutions of their salts these (seven) metals form metal ammonium compounds, all of which are soluble in water except the compounds of platinum and gold (highest in atomic weight). All of the seven named form sulphides insoluble in water, in condition of precipitation. For the most part their sulphides are relatively more stable than their oxides. Silver differs from the others in the insolubility of its chloride, and agrees irregularly in this fact, one prominent in analysis, with mercury in its lower valence, and partly with lead.

§11. *The Nitrogen Family of Elements.*—**N** 14.01, **P** 31.04, **As** 74.96, **Sb** 120.2, ——, **Bi** 208.0. These elements include the leading element of Group V., and the entire second part of the group. Nitrogen and phosphorus act as non-metals, antimony and bismuth as metals, while arsenic is intermediate, the polarity being more positive as the atomic weight increases. In combinations with hydrogen, like ammonia and ammonium compounds, phosphine and phosphonium salts, and also like analogous organic bases where carbo-hydrogen takes the place of a part or all of the hydrogen, there is a remarkable unity of type in this family. The same is true of the combinations with oxygen, like nitric acid. It is in Group V. that the group valence for oxygen begins to diverge in gradation from the group valence for hydrogen. While in ammonium compounds nitrogen exercises a valence of five, this total of five units is always limited in polarity to a balance of three negative units at most. In ammonia: $\mathbf{N^{-3}.HHH}$. In ammonium chloride: $\mathbf{N^{-4+1=-3}.HHHHCl}$. Bismuth is a distant member, a vacancy falling between it and antimony.

Phosphorus, arsenic and antimony are in gradation with each other as to their indifference to chemical combination and readiness of reduction to the elemental state, these qualities intensifying with the rise in atomic weight. In this gradation nitrogen, belonging among the other alternate members, has no part. In its chemical indifference it stands in extreme contrast to phosphorus.

§12. *Relation of Tin and Lead to the Nitrogen Family.*—These metals are in Group IV., having valences of four and five, differing from the valence of the nitrogen family. In Series 7: **Sn** 118.7 is closely related to **Sb** 120.2. In Series 11: **Pb** 207.20 is closely related to **Bi** 208.0. The metals in the first named pair are two removes from those in the second pair, all being among the second alternate members. In their salts tin and antimony are more easily subject to changes of valence than are lead and bismuth. In

further comarison, arsenic, in its deportment as a metal, may be included, making the list: **As** 74.96, **Sb** 120.2 (**Sn** 118.7), **Bi** 208.0 (**Pb** 207.20). Of these, only arsenic forms a higher oxide soluble in water (separation after treatment with nitric acid and evaporation). Arsenic and antimony form gaseous hydrides, in this agreeing with phosphorus and nitrogen, while the others do not. The stability of the hydrides of **N**, **P**, **As**, **Sb**, all in the type of ammonia, is in the ratio inverse to that of the atomic weight. All of these metals (**As, Sb, Sn, Bi, Pb**) are precipitable as hydroxides save arsenic, all are precipitated as sulphides, and these have chemical solubilities somewhat in gradation with atomic weights, the arsenic sulphide being most fully separable by chemical solvents. The sparing solubility of the chloride of lead, referred to in description of silver, is approached by the insolubility of the oxychlorides of bismuth, tin, and antimony, and this fact must be borne in mind, when precipitation by hydrochloric acid is employed for the separation of silver and univalent mercury in analysis.

Nitrogen in its trivalent union with hydrogen, the leading element of the group of alkali metals, constitutes an active alkali. In its prevalent union with oxygen, the leading element of Group VI., that is with oxygen and hydroxyl, nitrogen forms an acid which is very active though not very stable, its decomposition being represented by gunpowder. The degree of negative polarity of nitrogen, or its capacity for acid formation, in accordance with its place next to oxygen among the atomic weights, is shown in that singular unstable body, hydrazoic acid, HN_3 (also called azimide), of decided acid power, constituting well marked salts, such as sodium azoimide, NaN_3, in which a ring of nitrogen alone acts as an acid radical. The first four members of the nitrogen family agree with each other in forming trivalent and pentavalent anhydrides and acids, the pentavalent ones being the more stable. The pentavalent acids are of especial interest. In nitric acid the five units of positive valence of an atom of nitrogen are met by two atoms of oxygen with two units each of negative valence and a unit of negative valence of hydroxyl: $H—O—N\overset{=O}{\underset{=O}{}}$. The same constitution is found in metaphosphoric acid $HO\,P\,O_2$, meta-arsenic acid $HO\,As\,O_2$, and in antimonic acid $HO\,Sb\,O_2$. The so-called ortho acids, phosphoric and arsenic, have the constitution $(HO)_3\,P\,O$ and $(HO)_3\,As\,O$, respectively. Phosphoric and arsenic acids have a remarkable likeness to each other in nearly all the properties of all their salts, behaving alike in analysis so long as preserved from the action of reducing agents. These sharply separate arsenic, usually in one of its trivalent forms, AsH_3 or As_2S_3. Antimony is reduced from its acid even more readily than is arsenic, in accordance with the gradation stated above.

In the solubility of its salts with metals, the acid of nitrogen is, again, in

strong contrast with the acids of the elements of the second part, phosphoric and arsenic acids. Metal nitrates are generally all soluble in water. Of the metal phosphates and arsenates, that is the full metallic salts of phosphoric and arsenic acids, in their several forms, only those of the alkali metals dissolve in water.

§13. *The Halogens.*—**F** 19.00, **Cl** 35.46, **Br** 79.92, **I** 126.92. These metals constitute the leading elements of Group VII., and the three known members of the second alternates. In the halogen family fluorine has a relation like that of nitrogen in its family, taking part in the group gradation as to polarity, solubility of compounds and other qualities, but standing quite by itself in respect to certain properties. It is the most strongly electro-negative of the known elements, a fact in accord with the relation of its atomic weight.

For the common work of analysis we may confine our study of the halogens to chlorine, bromine, and iodine. In the order of their atomic weights, these elements appear, respectively, in gaseous, liquid, and solid state, under common conditions. Their hydrogen acids, **HCl**, **HBr**, and **HI**, show a stability in proportion to the electro-negative polarity of the halogen, hydriodic acid being so unstable as to suffer decomposition in the air. In the solubility of their metal salts these acids are nearly alike, all being soluble except the silver, univalent mercury, and lead salts, but the iodides of divalent mercury, bismuth and divalent palladium are sparingly soluble. Each of these halogens, most especially iodine, forms a class of salts each containing two metals, one of the united metals being that of an alkali, such as $(KI)_2\,HgI_2$ and $K_2\,Pt\,Cl_6$. The periodides show that iodine atoms have the power of uniting with each other, in the molecules of salts, a power partly shared by bromine and chlorine and probably exercised in many complex halogen compounds. By this means two atoms of a halogen may serve the same as one atom of oxygen, in the linkings of molecular structure.

Of the oxygen acids of chlorine, bromine and iodine, those in which the halogen has a valence of five are more stable than the others. These acids are chloric, $HO\,Cl\,O_2$; bromic, $HO\,Br\,O_2$; and iodic, $HO\,I\,O_2$. Chloric acid resembles nitric acid, $HO\,N\,O_2$, in the fact that it forms soluble salts with all the metals. Chlorates decompose more violently than nitrates; iodates for the most part less readily than the latter. Of the oxygen acids with a halogen valence of seven, periodic acid, $HO\,I\,O_3$, also $(HO)_5\,I\,O$, is preserved intact without difficulty. Perchloric acid is more stable than chloric acid.

§14. *The Relations of Sulphur.*—**S** 32.07. Sulphur is the first member of a family including selenium and tellurium. It differs from oxygen almost as much as phosphorus differs from nitrogen, and we may say more than silicon differs from carbon. The higher valence of Group VI., exer-

cised toward oxygen, cannot be met by oxygen itself. Of the acids of sulphur, H_2S, in which sulphur has two electro-negative units of valence, is quite unstable, while $(HO)_2SO_2$, in which the sulphur has six electro-positive units of valence, is the most stable. The sulphides (salts of H_2S) of the heavier metals quite generally are insoluble in water, an important means of separation in analysis. The sulphates (salts of H_2SO_4) of the larger number of the metals are soluble in water, the exceptions being important to observe, namely those of **Pb** 207.20, **Ba** 137.37, **Sr** 87.63, and (with sparing solubility) **Ca** 40.07. Of these sulphates, that of barium (least soluble), is the one usually employed in analytical separation.

§15. *The Relations of Carbon.*—**C** 12.0. Carbon, in a central position in respect to polarity, stands alone in its capacity for a multitude of distinct compounds with hydrogen and oxygen, with and without nitrogen, these being the so-called organic compounds. This capacity goes with the power of carbon atoms to unite with each other in the same molecule. It appears in acetylene C_2H_2 (H C≡C H), also in oxalic acid, (H O) O C—C O (O H). The same capacity of union of the atoms of an element with each other, in the molecules of compounds, is exercised by other elements in fewer instances, as by nitrogen in hydrazoic acid, by oxygen in ozone, by sulphur in thiosulphuric acid, and by iodine in periodides. In carbon, nitrogen, and oxygen we see a decreasing gradation of this capacity, as the atomic weights ascend. Silicon, next to carbon in Group IV., but in the opposite set of alternates, agrees with carbon in the formation of many corresponding compounds, and also exhibits to some extent the capacity of uniting its atoms to each other in building up combinations.

§16. The Classification of the Metals as Bases.

The object of the Periodic System is to group all the elements, both metallic and non-metallic, according to their general properties as related to their atomic weights. This has been briefly given in the foregoing pages for study bearing especially upon the main methods of analysis.

The ordinary grouping of the bases in the work of analysis, outlined in the next paragraph, is done by the action of a few chemical agents, termed "group reagents," which have been chosen from a large number of reagents, as being more satisfactory than others, for the use of the greater number of analysts. This ordinary grouping, therefore, is not the only way in which the metals can be separated, in the practice of analytical chemistry, nor is any one scheme of separation adopted throughout by all authorities. The principal separations of analysis can be well understood by gaining *an acquaintance with the properties of the leading bases and acids,*

in their action upon each other. Without this acquaintance, the analyst is the servant of routine, and his results liable to fallacy.

The following named are the bases of more common occurrence.

Metals Precipitated as Chlorides.

The Silver Group.

*The first group.**

Silver (Argentum).

† Ag^{I}: silver salts.

Mercury (Hydrargyrum).

Hg^{I}: mercurous salts.

Lead (Plumbum).

Pb^{II}: lead salts.

Silver and the mercury of mercurous salts can be removed as chlorides by precipitation with hydrochloric acid. The precipitate of lead is not insoluble enough to remove this metal entirely in separation from other groups.

Metals falling with Copper and Tin.

The second group.

Precipitated by H_2S **in acidulated solution.** (The precipitates are sulphides.)

The Tin Group.

Division A, second group.

Sn^{II}: stannous salts.

Sn^{IV}: stannic salts and stannates.

Sb^{III}: antimonous compounds.

Sb^{V}: antimonic compounds.

As^{III}: arsenous compounds.

As^{V}: arsenic compounds and arsenates.

Separated by dissolving the precipitated sulphides with Ammonium Sulphide.

The Copper Group.

Division B, second group.

Hg^{II}: mercuric salts.

Pb^{II}: lead salts.

Bi^{III}: bismuth salts.

Cu^{II}: copper or cupric salts.

Cu^{I}: cuprous salts.

Cd^{II}: cadmium salts.

Separated by the insolubility of the precipitated sulphides on treatment with Ammonium Sulphide.

* The first division of the bases, in the order in which they are separated from each other by precipitation with the group reagents.

† The Roman numerals (as ^{I}) express units of valence, each equivalent to an atom of hydrogen, in the formation of salts and other combinations.

The Iron Group. *The third group.* Fe^{II}: ferrous salts. Fe^{III}: ferric salts. Cr^{III}: chromic salts. Cr^{VI}: chromates. Al^{III}: aluminium salts.	*Separated by precipitation with* **Ammonium Hydroxide,** in presence of NH_4Cl, after the removal of previously named groups. (The precipitates are all hydroxides.)
The Zinc Group. *The fourth group.* Zn^{II}: zinc salts. Mn^{II}: manganous salts. Mn^{III}: manganic salts. Mn^{IV}: unstable salts. Mn^{VI}: salts of manganic acid. Mn^{VII}: salts of permanganic acid Ni^{II}: nickel salts. Co^{II}: cobaltous salts. Co^{III}: cobaltic salts.	*Separated by precipitation with* **Ammonium Sulphide,** *after removal of all previously named bases,* as directed above. (The precipitates are all sulphides.)
The Alkaline Earth Bases, *The fifth group.*	(Precipitated by carbonates, which fact alone does *not* separate them from the following named groups.)
Magnesium, Mg^{II}.	*Separated by precipitation as a* **phosphate** *after removing all the previously named bases.* Forms magnesium hydroxide, $Mg(OH)_2$, and magnesium salts, such as $MgSO_4$.
Calcium, Ca^{II}. Strontium, Sr^{II}. Barium, Ba^{II}.	*Separated by precipitation with* **Ammonium Carbonate,** *adding* NH_4Cl *to keep magnesium from precipitation.* Calcium carbonate, a normal salt, $CaCO_3$.
The Alkali Bases. *The sixth group.*	**Not precipitated** *from their salts by any of the group reagents.* Potassium and sodium are found after removing all the previously named groups. Ammonium is found by tests of the original, this base being added in the "group reagents."

Potassium (Kalium), K^{I}. In combination in potassium hydroxide, **KOH**, and in potassium salts, such as the chloride **KCl**, and the nitrate KNO_3.

Sodium (Natrium), Na^{I}. In the base, sodium hydroxide and its salts.

Ammonium $(NH_4)^{I}$. Forms ammonium hydroxide, NH_4OH, representing ammonia, NH_3, and water, and serving as the base of ammonium salts, such as $(NH_4)_2SO_4$, ammonium sulphate.

§17. THE ACIDS OF CERTAIN COMMONLY OCCURRING SALTS.

Name of Acid.	Name of Salt.	Formula.	Showing Hydroxyl.	Anhydride.
Carbonic	Carbonate	H_2CO_3	$(HO)_2C^{IV}O$	CO_2
Oxalic	Oxalate	$H_2C_2O_4$	$(HO)_2C_2^{IV}O_2$	C_2O_3
Nitric	Nitrate	HNO_3	$(HO)N^{V}O_2$	N_2O_5
Nitrous	Nitrite	HNO_2	$(HO)N^{III}O$	N_2O_3
Phosphoric (ortho)	Phosphate	H_3PO_4	$(HO)_3P^{V}O$	P_2O_5
Metaphosphoric	Metaphosphate	HPO_3	$(HO)P^{V}O_2$	P_2O_5
Pyrophosphoric	Pyrophosphate	$H_4P_2O_7$	$(HO)_4P^{V}_2O_3$	P_2O_5
Sulphuric	Sulphate	H_2SO_4	$(HO)_2S^{VI}O_2$	SO_3
Sulphurous	Sulphite	H_2SO_3		SO_2
Hydrosulphuric	Sulphide	H_2S		
Hydrochloric	Chloride	HCl		
Hydrobromic	Bromide	HBr		
Hydriodic	Iodide	HI		
Chloric	Chlorate	$HClO_3$	$(HO)Cl^{V}O_2$	Cl_2O_5
Iodic	Iodate	HIO_3	$(HO)I^{V}O_2$	I_2O_5

THE OPERATIONS OF ANALYSIS.

§18. Chemical analysis is the determination of any or all of the components of a given portion of matter, whether this be solid, liquid or gaseous. A portion of matter is made up of one or more definite and distinct substances, or chemical individuals, each of which is either a "compound" or an "element" and is always and everywhere the same. It is required in analysis to detect a chemical compound as a body distinct from the chemical elements that have formed it. For example, the analyst may have in hand a mixture containing sodium sulphate, Na_2SO_4; sodium sulphite, Na_2SO_3, and sodium thiosulphate, $Na_2S_2O_3$, but not containing any

sodium or sulphur or oxygen as these bodies are severally known to the world and described in chemistry. In this instance the analyst in his ordinary work does not separate the sulphur or the sodium, as elements uncombined with oxygen, either in qualitative or in quantitative operations. Each one of the *compounds* of the sulphur with the oxygen is usually sought for and found and weighed as a chemical individual. Certain of the chemical elements, however, are frequently separated free from all combination, as a method of determination of their compounds.

§19. The analysis of gaseous material is termed Gas Analysis; that of mixtures of the complex compounds of carbon, Organic Analysis. An examination of organic matter, when limited to a determination of its ultimate chemical elements is styled Ultimate Organic Analysis. When it is undertaken to determine individual carbon compounds actually existing in organic matter, it has been spoken of as Proximate Organic Analysis. If the same distinction were to be applied to inorganic analysis, we should have to say that it is mostly "proximate" but is sometimes "ultimate" in its methods of operation.

§20. The term Qualitative Chemical Analysis as commonly used is confined to a chemical examination of material, chiefly inorganic, in the solid or liquid state, the inquiry being limited for the most part to well known substances.

§21. In the methods of analysis of a mixture, it is often required to separate individual substances from each other, but sometimes a distinct compound can be identified and sometimes its quantity can be estimated while it is in the presence of other bodies. Both the identification and separation are accomplished, nearly always, by effecting changes, physical and chemical.

Methods of analysis are as numerous as are the ways of bringing into action the physical and chemical forces by which chemical changes are wrought. The characteristics of any chemical individual, by which it is distinguished and removed from others, lie in its responses to the physical and chemical forces, including especially the chemical action of certain well known compounds called reagents.

§22. The response toward **heat and pressure** fixes the melting and boiling points, its ordinary solid or liquid or gaseous state. The operations "in the dry way" are done over a flame or in a furnace, with or without solid "reagents" and with regard to oxidation. They represent some of the methods of metallurgical manufacture. The liquid state, whether by fusing or by solution, is the state commonly necessary or favorable to chemical change and its control.

§23. The deportment of a solid substance toward **light** comprises its color and that of its solutions, as well as that of its vapor, in ordinary light,

and the bands and primary colors it exhibits in the uses of the spectroscope (Crookes, *J. C.*, 1889, **55,** 255; Welsbach, *M.*, 1885, **6,** 47).

§24. The conduct of a chemical compound in *electrolysis* is, in various cases, a means both of identification and of separation. Electric *conductivity* methods are used for establishing the presence or absence of minute traces of substances (Kohlrausch Whitney, *Z. phys. Ch.*, 1896, **20,** 44). Again, traces of dissolved matters too minute for other means of detection can be revealed by the difference of *electric potential* between electrode and solution (Ostwald, *Lehrb.*, 2 Aufl., II, 1, 881; Behrend, *Z. phys. Ch.*, 1893, **11,** 466; Hulett, *Z. phys. Ch.*, 1900, **33,** 611).

§25. By far the most extensive of the resources of analysis lie in **the chemical reaction** of one definite and distinct substance with another, according to the character of each, giving rise to a chemical product having peculiarities of its own in evidence of its origin. In this way the compounds are bound in regular relations to each other. Therefore it belongs to the analyst to gain personal acquaintance with the behavior of the representative constituent bases and acids toward each other.

§26. Operations for chemical change are commonly conducted in **solution.** The material for analysis is dissolved, and is treated with reagents that are in solution. A solid or a gas is dissolved in a liquid in making a solution. When the dissolved substance is converted into one that will not dissolve a precipitate is formed. It is necessary therefore to understand the nature of solution and to give heed to its obvious limitations. Certain facts and conclusions as to the chemical state of dissolved compounds are presented under the head next following, "Solution and Ionization." But it must first be observed that the universal solvent, water, is always understood to be present in somewhat indefinite proportion in operations "in the wet way." It serves as a vehicle, as such not being included in any statement of the substances operated upon, nor formulated in equations, any more than is the material of the test tube, but often some portion of it enters into combination or suffers decomposition, and then it must be placed among the substances engaged in chemical change.

§27. No other property of substances has so great importance in analysis and in all chemical operations, as their **solubility in water.** It must never be forgotten that there are degrees of solubility, but there is hardly such a fact as absolute solubility, or insolubility, regardless of the proportion of the solvent. There are liquids which are miscible with each other in all proportions, but solids seldom dissolve in all proportions of the solvent, neither do gases. For every solid or gas, there is a least quantity of solvent which can dissolve it. One part of potassium hydroxide is soluble in one-half part of water (or in any greater quantity), but not in a less quantity of the solvent. One part of sodium chloride requires at least two

and a half parts of water to dissolve it. One part of mercuric chloride will dissolve in two parts of water at 100 degrees, but when cooled to 15 degrees so much of the salt recrystallizes from the solution, that it needs twelve parts more of water at the latter temperature to keep a perfect solution. Lead chloride dissolves in about twenty parts of hot water, about half of the salt separating from the solution when cold. Calcium sulphate dissolves in about 500 times its weight of water—this dilute solution forming one of the ordinary reagents. Barium sulphate is one of the least soluble precipitates obtained, requiring about 430,000 parts of water for its solution at ordinary temperature (Hollemann, *Z. phys. Ch.*, 1893, **12**, 131). In ordinary reactions it is not appreciably soluble in water. Lead sulphate dissolves in about 21,000 parts of water: in many operations this solubility may be disregarded, but in quantitative analysis the precipitate is washed with alcohol instead of water, losing less weight with the former solvent. These examples indicate the necessity of discriminating between degrees of solubility. Also the solubility of a particular compound is dependent upon the physical form of that compound (§**69**, 5 *b*); *e. g.*, amorphous magnesium ammonium phosphate is quite soluble in water, the crystalline salt being almost insoluble. The solubility of a solid is also dependent upon the size of the particles of the solid, a finely divided solid being more soluble than large particles of the same substance (Hullett and Allen, *J. Am. Soc.*, **24**, 667, 1902). In analysis it is customary to heat and then allow a precipitate to stand with the solution in which it was formed in order to obtain complete precipitation. When a solvent has dissolved all of a substance that it can at a particular temperature, in contact with the solid, the solution is said to be saturated at that temperature. It frequently happens that a saturated solution of a substance at a higher temperature may be cooled without separation of the solid. Such a solution (at the lower temperature) is said to be supersaturated and precipitation frequently is induced by jarring the solution, more surely by adding a crystal of the dissolved substance.

§**28.** The ordinary **liquid reagents** are water solutions—concentrated sulphuric acid and carbon disulphide being exceptions. Hydrochloric acid, liquid hydrogen sulphide, and ammonium hydroxide are solutions of gases in water; on exposure to the air these gases gradually separate from their solutions. All these gases escape much more rapidly when their solutions are warmed. The majority of liquid reagents are solids in aqueous solution. (See the list of Reagents.)

§**29.** Substances are said to dissolve in acids, or in alkalis, and this is termed **chemical solution**; more definitively it is chemical action and solution, the solution being counted as a physical change. We say that calcium oxide dissolves (chemically) in hydrochloric acid; that is, in the

reagent named hydrochloric acid, a mixture of that acid and water. The acid unites with the calcium oxide, forming a soluble solid, which the water dissolves. Absolute hydrochloric acid cannot dissolve calcium oxide.

§30. Solids can be obtained, without chemical change, from their aqueous solutions: Firstly, by evaporation of the water. This is done by a careful application of heat. Secondly, solids can be removed from solution, without chemical change, by (physical) precipitation—accomplished by modifying the solvent. If a solution of potassium carbonate, or of ferrous sulphate, be dropped into alcohol, a precipitate is obtained, because the salts will not dissolve, or remain dissolved, in the mixture of alcohol and water. But, in analysis, precipitation is more often effected by changing the dissolved substance instead of the solvent.

§31. Solids can be separated from their solution by precipitation due to chemical change, to the extent that the product is insoluble in the quantity of the solvent present. Calcium can be in part precipitated from not too dilute solutions of its salts, by addition of sulphuric acid; but there still remains not precipitated the amount of calcium sulphate soluble in the water and acid present, which is enough to give an abundant precipitate with ammonium oxalate, the precipitated sulphate being previously removed by filtration.

Time and heat are required for the completion of most precipitations. If it is necessary to remove a substance, by precipitation, before testing for another substance, the mixture should be warmed and allowed to stand for some time, before filtration. Neglect of these precautions often occasions a double failure; the true indication is lost, and a false indication is obtained.

§32. Reagents should be added in very small portions, generally drop by drop. Often the first drop is enough. Sometimes the precipitate redissolves in the reagent that produced it, and this is ascertained if the reagent be added in small portions, with observation of the result of each addition. If it is a final test, a quantity of precipitate which is clearly visible is sufficient, but if the precipitate is to be filtered out and dissolved, a considerable quantity should be formed. If the precipitate is to be removed and the filtrate tested further, the precipitation must be completed—by adding the reagent as long as the precipitate increases, with the warmth and time requisite in the operation; and a drop of the same reagent should be added to the filtrate to obtain assurance that the precipitation has been completed. It will be found, with a little experience, that some reagents must be used in relatively large quantities. On the contrary, the acids, sulphuric, hydrochloric and nitric, are required in a volume relatively very small.

§33. Certain very exact methods of identification can be conducted by drop tests upon a black or white ground, or upon a glass slide and especially

with the help of a **microscope** and with *studies of crystalline form*. Further see Behrens, *Z.* 1891, **30**, 125; and Herrnschmidt and Capelle, *Z.* 1893, **32**, 608.

§34. Precipitates are removed—usually by filtration, sometimes by decantation. If they are to be dissolved, they must be first washed till free from all the substances in solution. For complete precipitation some excess of the reagent must have been used. Beside the reagent there are other dissolved matters, after precipitations, some of which are indicated by the equation written for the change. All these dissolved substances permeate and adhere to the porous precipitate with greater or less tenacity. If they are not wholly washed away, some portion of them will be mixed with the dissolved precipitate. Then, the separation of substances, the only object of the precipitation, is not accomplished, while the operator, proceeding just as though it was accomplished, undertakes to identify the members of a group by reactions on a mixture of groups. The washing, on the filter, is best completed by repeated additions of small portions of water—around the filter border, from the wash bottle—allowing each portion to pass through before another is added. The washings should be tested, from time to time, until they are free from dissolved substances.

§35. In dissolving precipitates—by aid of acids or other agents—use the least possible excess of the solvent. Endeavor to obtain a solution nearly or quite saturated, chemically. If a large excess of acid is carried into the solution to be operated upon, it usually has to be neutralized, and the solution then becomes so greatly encumbered and diluted that reactions become faint or inappreciable. Precipitates may be dissolved on the filter, without excess of solvent, by passing the same portion of the (diluted) solvent repeatedly through the filter, following it once or twice with a few drops of water. The mineral acids should be diluted to the extent required in each case. For solution of small quantities of carbonates and some other easily soluble precipitates the acids may be diluted with fifty times their weight of water. Washed precipitates may also be dissolved in the test-tube, by rinsing them from the filter, through a puncture made in its point, with a very little water. If the filter be wetted before filtration, the precipitate will not adhere to it so closely.

§36. When a reagent is added in order to produce a change in the acid, alkaline or neutral condition of the solution, the addition of sufficient reagent to cause the desired change should always be governed by testing a drop of the solution, on a glass rod, with a piece of litmus paper.

§37. When substances in separate solution are brought together, an evidence of the formation of a new substance is the appearance of a solid in the mixture, i.e. a precipitate. A chemical change between dissolved substances—salts, acids, and bases—will be practically complete when one or

more of the products of such change is a solid or a gas, not soluble in the mixture. As an example, Calcium carbonate + Hydrochloric acid = Calcium chloride + Water + Carbon dioxide (gas).

§38. In the practice of qualitative analysis, the student necessarily refers to authority for the composition of precipitates and other products. For example, when the solution of a carbonate is added to the solution of a calcium salt, a precipitate is obtained; and it has been ascertained by quantitative analysis that this precipitate is normal calcium carbonate, $CaCO_3$, invariably. Were there no authorized statement of the composition of this precipitate, the student would be unable, without making a quantitative analysis, to declare its formula or to write the equation for its production. When the results of analytical operations are substances of unknown, uncertain, or variable composition, equations cannot be given for them.

§39. **The written equation** represents only the substances, and the quantity of each, which actually undergo the chemical change that is to be expressed. Thus, if a reagent is used to effect complete precipitation, an excess of it must be employed, beyond the ratio of its combining weight in the equation. That is, if magnesium sulphate be employed to precipitate barium chloride, the exact relative amount of magnesium sulphate indicated by the equation: $BaCl_2 + MgSO_4 = BaSO_4 + MgCl_2$, fails to precipitate all of the barium. The soluble sulphate must be in a slight excess. On the other hand, to effect complete precipitation of the sulphate the barium must be in a slight excess.

§40. By translating chemical equations into statements of proportional parts by weight, they are prepared to serve as standard data of absolutely pure materials, and applicable in operations of manufacture, with large or small quantities, after making due allowance for moisture and other impurities, necessary excess, etc. In quantitative analysis the equation is the constant reliance. For example, in dissolving iron by the aid of hydrochloric acid, we have the equation:

$$Fe + 2HCl = FeCl_2 + H_2 .$$
$$55.8 + 72.9 = 126.8 + 2 .$$

Also in precipitating ferrous chloride by sodium phosphate, we have the equation:

$$FeCl_2 + Na_2HPO_4,12H_2O = FeHPO_4 + 2NaCl + 12H_2O .$$
$$126.8 + (142.2 + 216) = 151.8 + 117 .$$

Suppose it is desired to determine from the above:

(1) How much hydrochloric acid, strength 32 per cent, is required to dissolve 100 parts of iron wire.

(2) What quantities of 32 per cent hydrochloric acid and iron wire are necessary to use in preparing 100 parts of absolute ferrous chloride.

(3) What materials and what quantities of them, may be used in preparing 100 parts of ferrous phosphate.

In practice allowance must be made for the facts that the iron wire will not be quite pure, and that a considerable excess of the hydrochloric acid would be necessary for the complete solution of the iron. Also that some excess of the phosphate would be necessary to the full precipitation of the iron. Irrespective of impurities, oxidation product and excess, the required quantities are found by the combining weights as follows:

1. $\begin{cases} 55.8/72.9 = 100/\mathbf{x} = \text{parts of absolute } \mathbf{HCl} \text{ for 100 parts of iron wire.} \\ 32/100 = \mathbf{x}/\mathbf{y} = \text{parts of 32 per cent } \mathbf{HCl} \text{ for 100 parts of iron wire.} \end{cases}$

2. $\begin{cases} 126.8/72.9 = 100/\mathbf{x}. \\ 32/100 = \mathbf{x}/\mathbf{y} = \text{parts of 32 per cent } \mathbf{HCl} \text{ for 100 parts of } \mathbf{FeCl_2}, \text{ absolute.} \\ 129.8/55.8 = 100/\mathbf{z} = \text{parts of iron wire for 100 parts of } \mathbf{FeCl_2}. \end{cases}$

3. $\begin{cases} 151.8/72.9 = 100/\mathbf{x}. \\ 32/100 = \mathbf{x}/\mathbf{y} = \text{parts of 32 per cent } \mathbf{HCl} \text{ for 100 parts of } \mathbf{FeHPO_4}. \\ 151.8/55\ 8 = 100/\mathbf{z} = \text{parts of metallic iron for 100 parts of } \mathbf{FeHPO_4}. \\ 151.8/358.2 = 100/\mathbf{u} = \text{parts of } \mathbf{Na_2HPO_4}, 12\mathbf{H_2O} \text{ for 100 parts of } \mathbf{FeHPO_4}. \end{cases}$

Practice in reducing the combining numbers of the terms in an equation to simple parts by weight, is a very instructive exercise, even in the early part of qualitative chemistry. It enforces correct and clear ideas of the significance of formulæ and equations, and refers all chemical expressions to the facts of quantitative work.

§41. The chief requirement in qualitative practice is an experimental acquaintance with the chemical relations of substances, rather than the identification of one after the other by routine methods. The acids and bases, the oxidizing and reducing agents, are all linked together in a network of relations, and the ability to identify one, as it may be presented in any combination or mixture, depends upon acquaintance with the entire fraternity.

§42. The full text of the book, rather than the analytical tables, should be taken as the guide in qualitative operations, especially in those upon known material. The tabular comparisons are commended to attention, especially for review. In actual analysis, the tables serve mainly as an index to the body of the work.

Solution and Ionization.

§43. The Theory of Electrolytic Dissociation, proposed by Arrhenius in 1887 (*Z. phys. Ch.*, 1887, **1**, 631), assumes that acids, bases and salts in water solution are present not as the intact molecule but split up into two or more parts called ions which are charged with negative or positive electricity. The facts upon which the theory is based are the osmotic pressure,*

* The pressure by virtue of which a soluble substance in contact with the solvent, as common salt in water, is enabled to rise against the force of gravity and distribute itself uniformly throughout the solvent, just as gas by the virtue of the gas-pressure occupies the entire space at its disposal.

lowering of the freezing point, raising of the boiling point and electrical conductivity of water solutions of acids, bases and salts. Because such water solutions conduct the electric current, acids, bases and salts are called electrolytes.

The osmotic pressure of a solution is believed to be proportional to the number of particles of the dissolved substance present in unit volume of the solution. In the case of non-electrolytes the osmotic pressure is proportional to the molecular weight; but the osmotic pressure of electrolytes is greater than corresponds to their molecular weight. This is readily explained by the assumption that some of the molecules are split into two or more parts.

In a similar manner the freezing point of a liquid is lowered by the presence of a dissolved substance, and the amount of the lowering is proportional to the number of dissolved particles. In the case of non-electrolytes the lowering is proportional to the molecular weight, but dissolved electrolytes depress the freezing point to a greater extent, indicating dissociation of the molecules. The boiling point of a liquid is raised by the presence of a dissolved substance, but this effect is greater in the case of electrolytes because the molecule is dissociated. This reasoning is similar to that applied to gas pressures.

The gas-laws (Boyle's, Guy-Lussac's, Henry's, and Dalton's) are found to hold for dissolved substances, osmotic pressure being substituted for gas-pressure (van 't Hoff, *Z. phys. Ch.*, 1887, **1**, 481; Morse and Frazer, *Am.*, **34**, 1 (1905); **37**, 324, 425, 558; **38**, 175 (1907); Lewis, *J. Am. Soc.*, **30**, 668 (1908)). Avogadro's Hypothesis is therefore applicable to solutions as well as to gases, and as abnormal gas-pressure points to dissociation in the gas (NH_4Cl, PCl_5) so excessive osmotic pressure, lowering of freezing point and raising of boiling point is taken as indicating dissociation of the dissolved substance. The osmotic pressure as well as the abnormal freezing and boiling point may be taken as a measure of this dissociation.

The fact that solutions of non-electrolytes do not conduct the electric current while solutions of electrolytes do conduct the electric current indicates that molecules are incapable of carrying the current, but that the component parts into which the molecule is split carry the current.

Faraday gave the name *ions* to the components of a substance conducting the electric current in solution. It is an observed fact that transmission of the current by a solution is always accompanied by movement of the ions in opposite directions (Hittorf, *Pogg.* 1853, **89**, 177). This is quite independent of any separations taking place at the electrodes. From this it is concluded that the ions carry the electricity from one pole to the other through the solution. If the ions are the carriers of electricity then the power of a solution to conduct the current will be in proportion to their

number, that is, to the extent of dissociation of the dissolved substance. And experiment shows that the dissociation calculated from the osmotic pressure is identical with the dissociation calculated from the electric conductivity.

Further, if in analysis of a substance in solution we are dealing not with the substance in its integrity but with certain ions, then our ordinary analytical reactions are reactions of the ions, and we may expect that where the substance for some reason is transformed from the ionized condition to the undivided molecule these reactions will fail. Here again the chemical activity will be proportional to the number of ions; and experiment shows that quantitative parallelism exists, to take the case of acids, between (1) the characteristic acid activity—the dissolving of metals, the influence as catalyzer on such changes as the inversion of cane-sugar and the saponification of esters; (2) the extent of dissociation as indicated by osmotic pressure, and (3) the extent of dissociation as indicated by electric conductivity. The same parallelism holds for other bodies in solution. A water solution of an acid such as hydrochloric or sulphuric should not be regarded as consisting of molecules of the acid and water but as a solution of molecules of **HCl** and the ions **H** and **Cl** or molecules of H_2SO_4 and ions **H** and SO_4, respectively, the hydrogen ion being charged with positive electricity and the acid ion with negative electricity. The very active acids and bases and the neutral salts undergo wide dissociation in water solution, while weak acids and bases retain almost entirely the non-dissociated condition, the strength of the acids being proportional to the concentration of the **H** ion.

The Electrolytic Dissociation Theory in its assumption of a separation into ions groups together and gives system and meaning to these three classes of facts, experimentally absolutely independent and up to Arrhenius' time without any suspected relationship. In each case the results calculated on the assumption of such a dissociation are in quantitative agreement with those obtained by measurement.

Corresponding in actual experience to the view that the common analytical reactions are due to the ions rather than to the molecule as a whole, is the analyst's practice of testing for acid radicle or basic radicle without regard to the other component. For instance, H_2S or K_2S will produce precipitates of metallic sulphides because the sulphur is present in solution as an ion. On the other hand HSO_4, H_2SO_3, or HSO_3 will not precipitate metals as sulphides, because in these acids the ion is composed of the sulphur and the oxygen present. Further, $HgCl_2$ in its chemical behavior is unlike other mercuric salts and unlike other chlorides. The mercury is not readily precipitated by alkali hydroxides nor is the chloride readily precipitated by silver salts. In agreement with this, its conductivity and osmotic pressure are also unlike those of the great

majority of neutral salts, both pointing to very slight dissociation into the ions. $CdCl_2$ is another neutral salt anomalous in that its conductivity and osmotic pressure are both low. And here also for precipitation of the chloride a considerable concentration of the reagent is necessary. Similar instances of the parallelism referred to are numberless.

§44. The Law of Mass-Action embodies the familiar principle that the chemical activity of a substance is proportional to its concentration. It was first recognized, although imperfectly, by Berthollet and was given mathematical expression by Guldberg and Waage in 1867. The latter investigators found it to accord well with the observed facts in some cases; in others there were wide discrepancies which were later shown by Arrhenius to disappear when the concentration, not of the reacting body as a whole but only of that part present in the ionized condition, was taken into consideration. We must assume that every chemical reaction is reversible, that is, that none of them proceed until the reacting substances are completely transformed. Then by a simple process of reasoning it is found that when equilibrium sets in the product obtained by multiplying together the concentrations of the reacting substances will be in a certain definite ratio to the product of the concentrations of the substances formed, concentration being defined as the quantity in unit volume.* For example, in the reaction indicated by the equation $CH_3CO_2H + C_2H_5OH = CH_3CO_2C_2H_5 + H_2O$, when equilibrium sets in $ab = kcd$, in which **a** and **b** are the concentrations of acid and alcohol respectively, **c** and **d** those of ester and water, while **k** is a constant peculiar to the reaction. Where the reaction is a dissociation, as with gaseous NH_4Cl, we have $ab = k'c$, **a** and **b** representing the concentrations of NH_3 and **HCl** respectively, **c** that of the undecomposed NH_4Cl, and **k′** the constant characteristic of this change. Dissociation into ions must follow the same laws, and for the electrolytic dissociation of acetic acid a similar equation holds, **a** and **b** in this case standing for concentration of **H** and acetic ions, **c** for concentration of non-dissociated acetic acid, while the constant is one governing only this particular dissociation. It is apparent from each of these equations that, if we add one of the products of the reaction and thus increase its concentration, the concentration of the other product must decrease in the same proportion—the extent of the reaction will be decreased; while, on the other hand, removing either or both of the products will tend to make the transformation complete. This deduction is of great significance. In making ethyl acetate from the acid and alcohol, in order to use the materials as completely as possible, the ester is distilled off as rapidly as produced

* The unit of quantity is the molecular weight taken in grams (the " mol "). Where there are 18.23 grams **HCl** in a liter either in solution or as gas the concentration is ½, where there are 72.92 grams in the same volume the concentration is 2 and so on.

while the water is taken up by some absorbent. Introducing gaseous NH_3 or HCl diminishes the dissociation of NH_4Cl by heat, and similarly adding either H ions or acetic ions will diminish the dissociation of acetic acid. Acetic acid is much weakened by the presence of a neutral acetate. A ferrous solution moderately acidified with acetic acid gives no precipitate on saturation with H_2S, but on addition of sodium acetate the black FeS is brought down. Similarly a weak base, as NH_4OH, is made still less effective by the presence of its strongly-dissociated neutral salt, as NH_4Cl. Quantitative agreement is obtained between observed effect of NH_4Cl on NH_4OH as saponifying agent and that calculated from the equation: $c_{NH_4} \cdot c_{OH'} = kc_{NH_4OH}$ (Arrhenius, *Z. phys. Ch.*, 1887, **1**, 110).

In general every acid is weakened by the addition of the neutral salt of the acid to its solution. Similarly bases are weakened by the addition of the neutral salt of the base to its solution.

§45. *The Solubility-Product.*—In the saturated solution which always remains after precipitation we have the usual dissociation equilibrium, as: $c_{Ag} \cdot c_{Cl'} = kc_{AgCl}$. Now the quantity of non-dissociated substance in a saturated solution is invariable and the right side of this equation is therefore constant. That is, in saturated solution the product of the concentrations of the ions is always the same for a given substance (Nernst). This Ostwald has called the Solubility-Product. Where the saturated solution is made by bringing the salt into contact with the solvent $c_{Ag} \cdot = c_{Cl'} \cdot$ From such a solution precipitation will take place on addition of either a silver salt or a chloride, for such addition largely increases the concentration of one ion and, to restore equilibrium, the concentration of the other ion must decrease in the same proportion, which is possible only by precipitation. From this follows the old empirical rule to add an excess of the reagent in making a precipitation. Experiments on this point give quantitative agreement with the theory (Nernst, *Z. phys. Ch.*, 1889, **4**, 372; Noyes, *Z. phys. Ch.*, 1890, **6**, 241; 1892, **9**, 603; 1898, **26**, 152).

The Solubility-Product of the alkaline-earth carbonates is $c_{M''} \cdot c_{CO_3''} = K$. In the solution of a neutral salt, as $CaCl_2$, Ca ions are present in large concentration. When a substance containing CO_3 ions in large concentration is added, as Na_2CO_3, the solubility-product is exceeded and precipitation takes place. Carbonic acid, however, is shown by conductivity and osmotic pressure measurements to be but slightly dissociated, that is, it contains few CO_3 ions, and in accord with this is the familiar fact that the alkaline earths are not precipitated by carbonic acid. Similarly the fixed alkali hydroxides, strongly dissociated, will precipitate

alkaline-earth hydroxides, while ammonium hydroxide, shown by other measurements to contain but few hydroxyl ions, will not.

For the metallic sulphides the solubility-product is $c_{M} \cdot c_{S''} = K$. The alkali sulphides as normal salts contain the **S** ion in large concentration and so produce precipitation even of the more soluble sulphides of the Iron and Zinc Groups. The slightly dissociated H_2S contains sufficient **S** ions to reach the solubility-product of the sulphides of the Silver, Tin, and Copper Groups, but not enough to attain to the larger solubility-product of the Iron and Zinc Group sulphides. A strong acid, as **HCl**, containing as it does **H** ions, one of the dissociation products of H_2S, drives back the dissociation of the H_2S, so decreasing the concentration of the **S** ions and making precipitation of the sulphide more difficult.

For the application of the dissociation theory to the details of analytical work we are indebted chiefly to Ostwald. See his "Scientific Foundations of Analytical Chemistry" and "Outlines of General Chemistry."

Order of Laboratory Study.

§46. The following is a suggestive outline to be modified by the teacher to suit the ability of the students, and the amount of time to be given to the study:

a. A review of chemical notation and the writing of the formulas of salts.

b. A study of the action of the **Fixed Alkalis** upon solutions of the salts of the metals in the order of their groupings; including the action of an excess of the reagent. The fact of the reaction should be stated; *e. g.*, the addition of potassium hydroxide to lead acetate produces a white precipitate readily soluble in excess of the reagent. The text should then be consulted for the products of the reaction (§57, 6*a*), and the reactions expressed in the form of equations:

$$2Pb(C_2H_3O_2)_2 + 4KOH = Pb_2O(OH)_2\,\text{* (white)} + 4KC_2H_3O_2 + H_2O$$

$$Pb_2O(OH)_2 + 4KOH\ \text{(excess)} = 2K_2PbO_2 + 3H_2O$$

or

$$Pb(C_2H_3O_2)_2 + 4KOH\ \text{(excess)} = K_2PbO_2 + 2KC_2H_3O_2 + 2H_2O.$$

The results should all be tabulated and then summarized in the form of a carefully worded generalization (§205, 6*a*).

c. Action of **Ammonium Hydroxide** (volatile alkali) upon solutions of the salts of the metals, etc., as in (*b*) above; *e.g.*, the addition of ammonium hydroxide to lead nitrate produces a white precipitate not dissolving in excess. Consult text (§57, 6*a*) and write the equation:

$$3Pb(NO_3)_2 + 4NH_4OH = \underline{2PbO \cdot Pb(NO_3)_2} + 4NH_4NO_3 + 2H_2O.$$

After the work has been completed in the laboratory and the results

* It has been found helpful to require students to underscore all precipitates.

discussed in the class room, summarize in the form of a generalized statement (§**207**, 6*a*).

d. A study of the action of the **Fixed Alkali Carbonates**, and generalization of the results (§**205**, 6*a*).

e. A study of the action of **Ammonium Carbonate**. Summarize the results (§**207**, 6*a*).

f. A study of the solvent action of acids, **HCl**, **HNO_3**, and **H_2SO_4**, upon the **Hydroxides** and **Carbonates** obtained by precipitation.

g. Action of **Hydrosulphuric Acid** as a precipitating agent upon salts of the metals in neutral and acid solutions.

h. The use of **Ammonium Sulphide** as a reagent.

i. The solvent action of acids, **HCl**, **HNO_3**, and **$HC_2H_3O_2$**, upon the sulphides obtained by precipitation.

j. Action of **Hydrochloric Acid** and **Soluble Chlorides**.
Action of **Hydrobromic Acid** and **Soluble Bromides**.
Action of **Hydriodic Acid** and **Soluble Iodides**.

k. Precipitation by **Soluble Sulphates, Phosphates**, and **Oxalates**.

l. The solvent action of **Hydrochloric** and **Acetic Acids** upon the **Phosphates** obtained by precipitation.

m. The reverse of certain of the above reactions as illustrating the precipitation of **Acids**; *e. g.*, the addition of calcium chloride to ammonium oxalate produces a white precipitate. Consult the text (§**227**, 8) and write the equation: **$(NH_4)C_2O_4 + CaCl_2 = CaC_2O_4 + 2NH_4Cl$**.

n. Application of the above reactions to the **Grouping** of the **Metals** for **Analysis.**

o. A study of the limit of visible precipitation with several reagents upon a particular metal, or upon a number of metals.

p. A study of the analysis of the individual metals and acids; combining them, and effecting their separation and detection. The new work should be followed by the analysis of "unknown" mixtures prepared by the teacher, to illustrate the new work and to give an instructive review of the preceding work. The order of the study of the metals and acids may be varied greatly. In no case should the metals of a whole group be studied without considering the relations to the other groups.

q. The study in the class room of **Oxidation** and **Reduction**, with work in the laboratory to illustrate.

r. The study of problems in **Synthesis** involving analytical separations, accompanied by laboratory experiments.

s. The analysis of a series of **Dry "Unknown" Mixtures.**

t. A special study of the analysis of **Phosphates, Oxalates, Borates, Silicates**, etc., and certain of the **Rarer Metals.**

u. The analysis of mixtures in solution, illustrating **Oxidation** and **Reduction.**

PART II.—THE METALS.

THE SILVER AND TIN AND COPPER GROUPS.

(First and Second Groups.)

§47. The Silver group (first group) includes the metals whose chlorides are insoluble in water and which are precipitated from solutions upon the addition of hydrochloric acid or soluble chlorides: **Pb, Hg′, Ag.**

The Tin and Copper group (second group) includes those metals whose sulphides are precipitated by hydrosulphuric acid from solutions acid with dilute hydrochloric acid, and whose chlorides (soluble in water for the most part) are not precipitated by hydrochloric acid or soluble chlorides.

Lead*	**Pb**	207.20	Germanium	**Ge**	72.5
Mercury	**Hg**	200.6	Iridium	**Ir**	193.1
Silver	**Ag**	107.88	Osmium	**Os**	190.9
Arsenic	**As**	74.96	Palladium	**Pd**	106.7
Antimony	**Sb**	120.2	Rhodium	**Rh**	102.9
Tin	**Sn**	118.7	Ruthenium	**Ru**	101.7
Gold	**Au**	197.2	Selenium	**Se**	79.2
Platinum	**Pt**	195.2	Tellurium	**Te**	127.5
Molybdenum	**Mo**	96.0	Tungsten	**W**	184.0
Bismuth	**Bi**	208.0	Vanadium	**V**	51.0
Copper	**Cu**	63.57			
Cadmium	**Cd**	112.4			

§48. Owing to the partial solubility of lead chloride in water, it is never completely precipitated in the first group; hence it must also be tested for in the second group. Monovalent mercury belongs to the first group and divalent mercury to the second. Silver, then, is the only exclusively first-group metal.

§49. The metals included in these groups are **less strongly electropositive** than those of the other groups. Only bismuth, antimony, tin, and molybdenum decompose water, and these only slowly and at high temperatures. The oxides of silver, mercury, gold, platinum, and palladium are decomposed below a red heat. Copper, lead, and tin tarnish by

* In this list of the metals of the Silver, Tin and Copper Groups the more common, those in the first column, are arranged in the order of their discussion and separation in analysis. The rare metals are arranged in alphabetic order, but are discussed in order of their relations to each other, beginning at § **104**.

oxidation in the air. In general, these metals do not dissolve in acids with evolution of hydrogen, or do so with difficulty. Nitric acid is the best solvent for all, except for antimony and tin, which are rapidly oxidized by it. Antimony may be dissolved by treatment with a little strong nitric acid and tartaric acid. The best solvent for tin is hot strong hydrochloric acid. Concerning the separation and detection of the metals of these groups by electrolysis, see Schmucker, *Z. anorg.*, 1894, **5**, 199, and Cohen, *J. Soc. Ind.*, 1891, **10**, 327 (§**12**).

§**50**. Mercury, arsenic, antimony, and tin form, each two stable classes of salts. Therefore, the lower oxides, chlorides, etc., of these metals act as reducing agents; and their higher oxides, chlorides, etc., as oxidizing agents, each to the extent of its chemical force. Arsenic, antimony, tin, molybdenum, and several of the rare metals of these groups enter into *acid* radicles, which form stable salts. Arsenic, selenium and tellurium are metalloids rather than metals. Arsenic, antimony, and bismuth belong to the Nitrogen Series of Elements.

§**51**. A large proportion of the compounds of these metals are **insoluble** in water. Of the oxides or hydroxides, only the acids of arsenic are soluble in water. The only insoluble chlorides, bromides, and iodides are in these groups. The sulphides, carbonates, oxalates, phosphates, borates, and cyanogen compounds are insoluble. Most of the so-called soluble compounds of bismuth, antimony, and tin, and some of those of mercury, dissolve only in acidulated water, being decomposed by pure water, with formation of insoluble basic salts.

§**52**. Among the many soluble double salts of the metals of these groups are especially to be mentioned the double iodides with **KI** and the iodides of **Pb**, **Hg**, **Ag**, **Bi** and **Cd**. Platinum forms a large number of stable double chlorides, soluble and insoluble; and gold forms double chlorides, cyanides, etc.

§**53**. The oxides of arsenic act as acid anhydrides and form soluble salts with the alkalis; oxides of antimony, tin, and lead, are soluble in the fixed alkalis; oxides of silver, copper, and cadmium, in ammonium hydroxide. Metallic lead, like zinc, dissolves in the fixed alkalis with evolution of hydrogen.

§**54**. The solubility of certain sulphides in the alkali sulphides forming sulpho salts or double sulphides, separates the metals of the second group into two divisions. *A* (copper group)—**Hg**, **Pb**, **Bi**, **Cu**, **Cd**, **Os**, **Pd**, **Rh**, and **Ru**; sulphides not soluble in yellow ammonium sulphide: and *B* (tin group)—**As**, **Sb**, **Sn**, **Ge**, **Au**, **Ir**, **Mo**, **Pt**, **Se**, **Te**, **W**, and **V**; sulphides soluble in yellow ammonium sulphide.

§**55**. Mercury, antimony, silver, and gold do not form hydroxides. The oxides of gold are very unstable.

§**56**. The metals of these groups are all easily reduced to the metallic state by ignition on charcoal. Except mercury and arsenic, which vaporize

readily, and certain rarer metals difficultly fusible, the reduced metals melt to metallic grains on the charcoal.

The Silver Group (First Group).

Lead, Mercury (Mercurosum), Silver.

§57. Lead (Plumbum Pb = 207.20. Valence two and four.

1. **Properties.**—*Specific gravity*, 11.34 (Reich, *J. pr.*, 1859, **78**, 328). *Melting point*, 327.4°. B. S., circular No. 35, 2nd ed., 1915. Vaporization is said to take place at 360° (Demarcay, *C. r.*, 1882, **95**, 183). Boiling point about 1525° (H. C. Greenwood, *C. N.*, **39**, 49). It can be distilled in vacuo, (Schuller, *B.*, 1883, **16**, 1312).

Pure lead is almost white, soft, malleable, very slightly ductile; freshly cut surfaces tarnish in the air from formation of a film of oxide. The presence of traces of most of the other metals makes lead sensibly harder. It is a poor conductor of heat and electricity, and forms alloys with most metals; lead and tin in various proportions form solder and pewter; lead and arsenic form shot metal; lead and antimony, type metal; lead, bismuth, tin and cadmium form easily fusible alloys of low melting points (minimum 55.5°; *Ch. Z.*, **30**, 1139–1143; *J. Soc. Ind.*, **25**, 1221).; bell metal consists of tin, copper, lead and zinc.

2. **Occurrence.**—It is rarely found native (Chapman, *Phil. Mag.*, 1886, (4), **31**, 176); the most abundant lead mineral is galena, **PbS**; it also occurs as cerussite, $PbCO_3$; anglesite, $PbSO_4$; pyromorphite, $Pb_5Cl(PO_4)_5$; crocoite, $PbCrO_4$; and in many other minerals in combination with arsenic, antimony, etc. The United States produces more lead than any other country. Spain produces about one-fourth of the world's supply.

3. **Preparation.**—(*a*) From argentiferous lead ores; after roasting, if necessary, the ore is smelted in a rectagular blast furnace with a properly proportioned mxiture of coke and limestone. The lead (base bullion) produced is desilverized and refined by the Betts (electrolytic) process, or desilverized by the Parkes process and subsequently refined in a reverberatory furnace. (*b*) From galena, by the roast-reaction process in reverberatory furnaces, and ore hearths; the ore is roasted with access of air, forming variable quantities of $PbSO_4$, **PbO**, and **PbS**. Air is then excluded and the temperature raised, the sulphur of the sulphide then reduces both oxide and sulphate with formation of SO_2:

$$PbSO_4 + 2PbO + 2PbS = 5Pb + 3SO_2$$

In variations of this process carbon is used to aid in the reduction.

4. **Oxides.**—Lead forms four oxides, Pb_2O, **PbO**, PbO_2, and Pb_3O_4. *Lead suboxide* (Pb_2O) is little known: it is the black powder formed when PbC_2O_4 is heated to 300°, air being excluded. *Lead oxide* (litharge, or massicot) is formed by intensely igniting in the air **Pb**, Pb_2O, PbO_2, Pb_3O_4, $Pb(OH)_2$, $PbCO_3$, PbC_2O_4, or $Pb(NO_3)_2$. It has a yellowish-white color, melts at a red heat, and is volatile at a white heat.

Trilead tetroxide (red lead or minium), Pb_3O_4, is formed by heating **PbO** to a dull-red heat with full access of air for several hours. Strong, non-reducing acids, such as HNO_3, H_2SO_4, $HClO_3$, etc., convert it into a lead salt and PbO_2 (*a*). But concentrated hot H_2SO_4 converts the whole into $PbSO_4$, oxygen being evolved (*b*). But with the dilute acid and reducing agents, such as $C_3H_5(OH)_3$, $C_6H_{12}O_6$, $H_2C_2O_4$, $H_2C_4H_4O_6$, **Zn**, **Al**, **Cd**, **Mg**, **As**, **Pb**, etc., it is all reduced to the *dyad lead* without evolution of oxygen (*c*), (*d*), and (*e*). Hydracids usually reduce the lead and are themselves oxidized (*f*).

(*a*) $Pb_3O_4 + 2H_2SO_4$ (dilute) $= PbO_2 + 2PbSO_4 + 2H_2O$

(*b*) $2Pb_3O_4 + 6H_2SO_4$ (concentrated and hot) $= 6PbSO_4 + 6H_2O + O_2$

(*c*) $Pb_3O_4 + H_2C_2O_4 + 6HNO_3 = 3Pb(NO_3)_2 + 4H_2O + 2CO_2$

(*d*) $10Pb_3O_4 + As_4 + 30H_2SO_4 = 30PbSO_4 + 4H_3AsO_4 + 24H_2O$

(*e*) $Pb_3O_4 + Zn + 4H_2SO_4 = 3PbSO_4 + ZnSO_4 + 4H_2O$

(*f*) $Pb_3O_4 + 8HCl = 3PbCl_2 + Cl_2 + 4H_2O$

The *valence* of Pb_3O_4 is best explained by the theory that it is a union of the dyad and tetrad (Pb'' and Pb^{IV}), $Pb_3O_4 = 3PbO + Pb^{IV}O_2$.

Lead dioxide or *peroxide*, PbO_2, is formed: (1) by fusion of PbO with $KClO_3$ or KNO_3; (2) by fusing Pb_3O_4 with KOH; (3) by treating any compound of Pb″ with Cl, Br, $K_3Fe(CN)_6$, $KMnO_4$, or H_2O_2 in presence of KOH; (4) by treating Pb_3O_4 with non-reducing acids:

$$Pb_3O_4 + 4HNO_3 = PbO_2 + 2Pb(NO_3)_2 + 2H_2O.$$

Ignition forms first Pb_3O_4 and above a red heat PbO, oxygen being given off. It dissolves in acids on same conditions as Pb_3O_4. Very strong solution of potassium hydroxide, in large excess, dissolves it, with formation of "potassium plumbate," K_2PbO_3. Lead dioxide is a powerful oxidizing agent, one of the strongest known. Digested with ammonium hydroxide, it forms lead nitrate and water. Triturated with one-sixth of sulphur, or tartaric acid, or sugar, it takes fire; with phosphorus, it detonates.

5. **Solubilities.**—*a. Metal.*—Nitric acid is the proper solvent for metallic lead, the lead nitrate formed is readily soluble in water but insoluble in concentrated nitric acid*; hence if the concentrated acid be used to dissolve the lead, a white residue of lead nitrate will be left which dissolves on the addition of water. If concentrated and hot, the nitric acid is reduced to NO which, on contact with the oxygen of the air, becomes N_2O_3 (§241, 6). The reactions are as follows:

$$3Pb + 8HNO_3 = 3Pb(NO_3)_2 + 2NO + 4H_2O \qquad 4NO + O_2 = N_2O_3.$$

Dilute sulphuric acid is without action, the concentrated acid is almost without action in the cold (Calvert and Johnson, *J. C.*, 1863, **16**, 66), but the hot concentrated acid slowly changes the metal to the sulphate with evolution of sulphur dioxide, a portion of the salt being dissolved in the acid, precipitating on the addition of water. The following reaction takes place (§266, 6A):

$$Pb + 2H_2SO_4 = PbSO_4 + SO_2 + 2H_2O.$$

Hydrochloric acid very slowly dissolves the metal (more rapidly when warmed), evolving hydrogen; the chloride formed dissolves in the acid in quantities depending upon conditions of temperature and concentration (*c*). The halogens readily attack the metal forming the corresponding haloid salts. Alloys of lead are best dissolved by first treating with nitric acid; if a white residue is left it is washed with water and, if not dissolved, it is then treated with hydrochloric acid, in which it will usually be soluble.

Water used for drinking or cooking purposes should not be allowed to stand in lead pipes. Pure water free from air is without action upon pure lead, but water containing air and carbon dioxide very slowly attacks lead, forming the hydroxide and basic carbonate. This action is promoted by the presence of salts, as ammonium nitrate, nitrite, chloride, etc.; the action seems to be hindered by the presence of sulphates.

b. Oxides.—**Lead oxide**, *litharge*, PbO, and the hydroxides, $2PbO.H_2O$; $3PbO.H_2O$, are readily dissolved or transposed by acids forming the corresponding salts, *i. e.*, $PbO + H_2SO_4 = PbSO_4 + H_2O$. The oxide and hydroxide are soluble in about 7000 parts of water, to which they impart an alkaline reaction. They are soluble in the fixed alkalis forming plumbites; soluble in certain salts as NH_4Cl, $CaCl_2$, and $SrCl_2$ (André, *C. r.*, 1883, **96**, 435; 1887, **104**, 359); very soluble in lead acetate, forming a strongly alkaline solution of basic lead acetate.

Lead dioxide, PbO_2, *lead peroxide*, is insoluble in water or nitric acid; it is dissolved by the halogen hydracids with liberation of the halogen and reduction of the lead forming a dyad salt: $PbO_2 + 4HCl = PbCl_2 + Cl_2 + 2H_2O$; it is attacked by hot concentrated sulphuric acid, forming the sulphate and liberating oxygen; it is soluble in glacial acetic acid forming $Pb(C_2H_3O_2)_4$, unstable (Hutchinson and Pollard, *J. C.*, 1896, **69**, 212). Some of the salts of the tetrad lead seem to be formed when the peroxide is treated with certain acids in the cold. They are, however, very unstable, being decomposed to the dyad salt upon warming (Fischer, *J. C.*, 1879, **35**, 282; Nickels, *A. Ch.*, 1867, (4), **10**, 328). The peroxide is slowly soluble in the fixed alkali hydroxides forming plumbates, *i. e.*, $PbO_2 + 2KOH = K_2PbO_3 + H_2O$.

Trilead tetroxide, Pb_3O_4, *red lead*, *minium*, is insoluble in water, is attacked by nearly all acids in the cold forming the corresponding dyad lead

* The solubility of a salt is lessened by the presence of another substance having an ion in common with it (§ 45). In some cases, as with PbI_2 and KI, this is offset in concentrated solution by the formation of a complex compound.

salt and ead peroxide, PbO_2. Upon further treatment with the acids using heat the lead peroxide is decomposed as described above. The presence of many reducing agents, as alcohol, oxalic acid, hydrogen peroxide, etc., greatly facilitates the solution of red lead or lead peroxide in acids, *i. e.*, nitric acid does not dissolve lead peroxide, but if a few drops of alcohol be added the solution is readily obtained upon warming, the lead being reduced and then converted into the soluble nitrate.

c.—Salts.—The carbonate, borate, cyanide, ferrocyanide, phosphate, sulphide, sulphite, iodate, chromate, and tannate are insoluble in water. The sulphate is soluble in about 21,000 parts of water at 18° (Kohlrausch and Rose, *Z. phys. Ch.*, 1893, **12**, 241), the presence of HNO_3 or **HCl** increasing its solubility in water; it is insoluble in alcohol even when quite dilute; sparingly soluble in concentrated H_2SO_4, from which solution it is precipitated by the addition of water or alcohol; *less soluble in dilute* H_2SO_4 *than in water*; soluble in 682 parts 10 per cent **HCl**, in 35 parts 31.5 per cent (Rodwell, *J. C.*, 1862, **15**, 59); transposed and dissolved by excess of **HCl**, **HBr**, or **HI** forming the corresponding haloid salt; insoluble in **HF** (Ditte, *A. Ch.*, 1878, (5), **14**, 190); soluble in ammonium sulphate, nitrate, acetate, tartrate and citrate, and from these solutions not readily precipitated by ammonium hydroxide or sulphate (Fleischer, *J. C.*, 1876, **29**, 190; Woehler, *A.*, 1840, **34**, 235). The sulphate is almost completely transposed to the nitrate by standing several days with cold concentrated nitric acid (Rodwell, *l. c.*). The oxalate is sparingly soluble in water, insoluble in alcohol. The ferricyanide is very slightly soluble in cold water, more soluble in hot water. The chloride is soluble in 85 parts water at 20° and in 32 parts at 80° (Ditte, *C. r.*, 1881, **92**, 718). The bromide is soluble in 166 parts water at 10°, in about 45 parts at 80°. The iodide is soluble in 1235 parts water at ordinary temperature, and in 194 parts at 100° (Denot, *J. pr.*, 1834, **1**, 425). The chloride is less soluble in dilute **HCl** or H_2SO_4 than in water, but is more soluble in the concentrated acids (Ditte, *l. c.*); HNO_3 increases the solubility of the chloride more and more as the HNO_3 is stronger. The chloride is less soluble in a solution of **NaCl** than in water (Field, *J. C.*, 1873, **26**, 575); soluble in NH_4Cl —90 grams dissolving in 200 grams NH_4Cl with 200 cc. water (André, *C. r.*, 1893, **96**, 435). The chloride, bromide, and iodide are insoluble in alcohol. The iodide is moderately soluble in solutions of alkali iodides; it is decomposed by ether. The basic acetates are permanently soluble if carbonic acid is strictly excluded. The basic nitrates are but slightly soluble in water, and are precipitated on adding solutions of KNO_3 to a solution of basic lead acetate.

The relative insolubility of $PbCl_2$ in cold water or in dilute **HCl** makes it possible to precipitate the most of the lead (by means of **HCl**) from solutions containing also the other metals of the *Silver Group;* while its solubility in hot water is the means of its separation from the other chlorides of that group (§**61**). The lead is separated and identified in the second group as the insoluble sulphate. (§**95**).

6. **Reactions.** *a.*—**Fixed alkali hydroxides** precipitate, from solutions of lead salts, *basic lead hydroxide* (*1*), $Pb_2O(OH)_2$ (Schaffner, *A.*, 1844, **51**, 175), white, soluble * in excess of the reagent as plumbite (*2*) (distinction from silver, mercury, bismuth, copper, and cadmium). The normal lead hydroxide, $Pb(OH)_2$, may be formed by adding a solution of a lead salt to a solution of a fixed alkali hydroxide.

(*1*) $2Pb(NO_3)_2 + 4KOH = Pb_2O(OH)_2 + 4KNO_3 + H_2O$

(*2*) $Pb_2O(OH)_2 + 4KOH = 2K_2PbO_2 + 3H_2O$.

Ammonium hydroxide precipitates white basic salts, insoluble in water and in excess of the reagent (distinction from silver, copper, and cadmium); with the chloride the precipitate, insoluble in water, is $PbCl_2.PbO.H_2O$ (Wood and Bordeu, *C. N.*, 1885, **52**, 43); with the nitrate $2PbO.Pb(NO_3)_2$ (*D.*, **2**, 2, 558). With the acetate, in solutions of ordinary strength, excess of ammonium hydroxide (free from carbonate) gives no precipitate, the soluble tribasic acetate being formed.

Alkali carbonates precipitate *basic lead carbonate, white*, the composition varying with the conditions of precipitation. With excess of the reagent and in hot concentrated solutions the precipitate consists chiefly of $Pb_3(OH)_2(CO_3)_2$. Precipitation in the cold approaches more nearly to the normal carbonate (Lefort, *Pharm. J.*, 1885, (3), **15**, 26). Solutions of lead salts when boiled with freshly precipitated *barium carbonate* are completely precipitated. Carbon dioxide precipitates the basic acetate but not completely.

b.—**Oxalic acid** and **alkali oxalates** precipitate lead *oxalate*, PbC_2O_4, *white*, from solutions of lead salts, soluble in nitric acid, insoluble in acetic acid. A solution of **lead acetate** precipitates a large number—and a solution of **lead subacetate** a still larger number—of organic acids, color substances, resins, gums, and neutral principles. Indeed it is a rule, with few exceptions, that lead subacetate removes organic acids (not formic, acetic, butyric, valeric, or lactic). Tannic acid precipitates solutions of lead acetate, and of the nitrate incompletely, as yellow-gray lead tannate, soluble in acids.

Soluble **cyanides** precipitate *lead cyanide*, $Pb(CN)_2$, white, sparingly soluble in a large excess of the reagent and reprecipitated on boiling. Potassium ferrocyanide precipitates lead ferrocyanide, $Pb_2Fe(CN)_6$, white, insoluble in water or dilute acids. Potassium ferricyanide precipitates from solutions, not too dilute, lead ferricyanide, $Pb_3(Fe(CN)_6)_2$, white, sparingly soluble in water, soluble in nitric acid. Solutions of lead salts are precipitated by potassium sulphocyanate as lead sulphocyanate, $Pb(CNS)_2$, white, soluble in excess of the reagent and in nitric acid.

c.—Lead nitrate is very soluble in water, the solution dissolving the oxide to form a basic nitrate, which may also be formed by precipitating lead acetate with

* Nearly all the salts are soluble in the fixed alkali hydroxides, PbS forming almost the only notable exception.

potassium nitrate. The solubility of lead nitrate is greatly increased by the presence of the nitrates of the alkalis and of the alkaline earths, a complex compound being formed (Le Blanc and Noyes, *Z. phys. Ch.*, 1890, **6**, 385).

d.—The higher oxides of lead are all reduced by *hypophosphorous* acid, lead phosphate being formed. Lead phosphite, $PbHPO_3$, white, is formed by nearly neutralizing phosphorous acid with lead carbonate or precipitating Na_2HPO_3 with $Pb(NO_3)_2$ (Amat, *C. r.*, 1890, **110**, 901). **Sodium phosphate**, Na_2HPO_4, precipitates from solutions of lead acetate the *tribasic lead phosphate*, $Pb_3(PO_4)_2$, white, insoluble in the acetic acid which is set free (*D.*, **2**, 2, 562): $3Pb(C_2H_3O_2)_2 + 2Na_2HPO_4 = Pb_3(PO_4)_2 + 4NaC_2H_3O_2 + 2HC_2H_3O_2$. The same precipitate is formed when sodium phosphate is added to lead nitrate, soluble in nitric acid, insoluble in acetic acid. Lead phosphate is also precipitated upon the addition of phosphoric acid to solutions of lead acetate or lead nitrate. The *pyrophosphate*, $Pb_2P_2O_7$, white, amorphous, is formed by precipitating a lead solution with $Na_4P_2O_7$, soluble in excess of the precipitant, in nitric acid, and in potassium hydroxide; insoluble in ammonium hydroxide and in acetic acid (Gerhardt, *A. Ch.*, 1849, (3), **25**, 305). The metaphosphate, $Pb(PO_3)_2$, white, crystalline, is obtained by the action of $NaPO_3$ upon $Pb(NO_3)_2$ in excess.

e.—**Hydrosulphuric acid** and the **soluble sulphides** precipitate—from neutral, acid, or alkaline solutions of lead salts—*lead sulphide*, **PbS**, brownish black, insoluble in dilute acids, in alkali hydroxides, carbonates, or sulphides. Freshly precipitated **CdS**, **MnS**, **FeS**, **CoS**, and **NiS** also give the same precipitate. Hydrosulphuric acid and the soluble sulphides transpose all freshly precipitated lead salts to lead sulphide.* Moderately dilute nitric acid—15 to 20 per cent—dissolves lead sulphide with separation of sulphur (*1*), some of the sulphur, especially if the nitric acid be concentrated, is oxidized to sulphuric acid, which precipitates a portion of the lead (*2*), unless the nitric acid be sufficiently concentrated to hold that amount of lead sulphate in solution. The oxidation of sulphur always occurs when nitric acid acts upon sulphides, and in degree proportional to the strength of acid, temperature, and duration of contact.

(*1*) $6PbS + 16HNO_3 = 6Pb(NO_3)_2 + 3S_2 + 4NO + 8H_2O$

(*2*) $3PbS + 8HNO_3 = 3PbSO_4 + 8NO + 4H_2O$

In solutions too strongly acidulated, especially with hydrochloric acid, either no precipitation takes place, or a brick-red double salt, Pb_2SCl_2,

* The condition for equilibrium is that a certain ratio of concentration exist between the ions, in the case of $PbSO_4$ between the S ions and the SO_4 ions. These concentrations are the same as those in a solution obtained by digesting the two salts, $PbSO_4$ and PbS, together in water. $PbSO_4$ dissolves more freely than PbS, and for equilibrium therefore $^{c}_{SO_4''}$ must be correspondingly greater than $^{c}_{S''}$. But adding H_2S or a soluble sulphide to $PbSO_4$ gives just the opposite of this condition, and transformation accordingly results, increasing the SO_4'' concentration by formation of soluble sulphate and decreasing the S'' concentration by precipitation of PbS, until the equilibrium-ratio is produced or, if the quantity of $PbSO_4$ present is insufficient for this, until all the $PbSO_4$ has been transformed to sulphide. On the other hand, treatment of PbS with a very large excess of H_2SO_4 will cause the reverse action, S ions going into solution until the same equilibrium results as before.

The general principle is then that unless a constituent of the more soluble substance is in great preponderance in the solution the least soluble of two or more possible products will always be formed. This principle determines the direction in which a reaction takes place; $AgCl + KI = AgI + KCl$; $CaSO_4 + Na_2CO_3 = CaCO_3 + Na_2SO_4$ (§44).

is formed, the precipitation being incomplete. In neutral solutions containing 100,000 parts of water lead is revealed as the sulphide; a test which is much more delicate than the formation of the sulphate.

Ferric chloride decomposes lead sulphide, forming lead chloride, ferrous chloride and sulphur. The reaction takes place in the cold and rapidly when warmed (Gabba, *C. C.*, 1889, 667).

When galena, **PbS**, is pulverized with fused **$KHSO_4$**, **H_2S** is evolved (Jannettaz, *J. C.*, 1874, **27**, 188).

Lead thiosulphate, **PbS_2O_3**, white, is precipitated by adding **sodium thiosulphate** to solutions of lead salts; the precipitate is readily dissolved in an excess of the reagent, forming the double salt, **$PbS_2O_3.2Na_2S_2O_3$** (Lenz, *A.*, 1841, **40**, 94); on boiling, all the lead is slowly precipitated as sulphide (Vohl, *A.*, 1855, **96**, 237).

Sodium **sulphite** precipitates *lead sulphite*, **$PbSO_3$**, white, less soluble in water than the sulphate, slightly soluble in sulphurous acid; decomposed by sulphuric, nitric, hydrochloric, and hydrosulphuric acids and by alkali sulphides; not decomposed by cold phosphoric and acetic acids.

Sulphuric acid and soluble **sulphates** precipitate from neutral or acid solutions, *lead sulphate*, **$PbSO_4$**, white, not readily changed or permanently dissolved by acids, except hydrosulphuric acid, yet slightly soluble in strong acids (*5c*). Soluble in the fixed alkalis and in most ammonium salts, especially the acetate, tartrate, and citrate (Woehler, *A.*, 1840, **34**, 235). Soluble in warm sodium thiosulphate solution, in hot solution decomposed, lead sulphide, insoluble in thiosulphate, being formed (distinction and separation from barium sulphate, which does not dissolve in thiosulphates).

The test for lead as a sulphate is from five to ten times less delicate than that with hydrosulphuric acid; but lead is *quantitatively* separated as a sulphate, by precipitation with sulphuric acid in the presence of alcohol, and washing with alcohol. When heated with potassium chromate transposition takes place and yellow lead chromate is formed (*h*). Excess of potassium iodide transposes lead sulphate (*f*), a distinction of lead from barium. Repeated washing of lead sulphate with a solution of sodium chloride completely transposes the lead to the chloride (Matthey, *J. C.*, 1879, **36**, 124). See footnote on previous page.

f.—**Hydrochloric acid** and soluble **chlorides** precipitate, from solutions not too dilute, *lead chloride*, **$PbCl_2$**, white. This reaction constitutes lead a member of the **FIRST GROUP**—as it also is of the second. The solubility of the precipitate is such (*5c*) that the filtrate obtained in the cold gives marked reactions with hydrosulphuric acid, sulphuric acid, chromates, etc.; and that it can be quite accurately separated from silver chloride and mercurous chloride by much hot water. Also, small proportions of lead escape detection in the first group, while its *removal is necessarily accomplished in the second group.*

Hydrobromic acid and soluble **bromides** precipitate *lead bromide*, $PbBr_2$, white, somewhat less soluble in water than the chloride (*5c*); soluble in excess of concentrated potassium bromide, as $2KBr.PbBr_2$, which is decomposed and $PbBr_2$ precipitated by dilution with water.

Hydriodic acid and soluble **iodides** precipitate *lead iodide*, PbI_2, bright yellow and crystalline, much less soluble in water than the chloride or bromide (*5c*); soluble in hot moderately concentrated nitric acid and in solution of the fixed alkalis; soluble in excess of the alkali iodides, by forming double iodides, $KIPbI_2$ with small excess of **KI**, and $4KI.PbI_2$ with greater excess of **KI**; these double iodides are decomposed by addition of water with precipitation of the lead iodide. Lead iodide is not precipitated in presence of sodium citrate; alkali acetates also hold it in solution to some extent, so that it is less perfectly precipitated from the acetate than from the nitrate. Freshly precipitated lead peroxide, PbO_2, gives free iodine when treated with potassium iodide (Ditte, *C. r.*, 1881, **93**, 64 and 67).

In detecting lead as an iodide in solutions of the chloride by precipitation with potassium iodide and recrystallization of the yellow precipitate from hot water, care must be taken that the potassium iodide be not added in excess to form the soluble double iodides.

g.—**Arsenous acid** does *not* precipitate neutral solutions of lead salts; from alkaline solutions or with soluble **arsenites** a bulky white precipitate of *lead arsenite* is formed, insoluble in water, but readily soluble in all acids and in the fixed alkali hydroxides. **Arsenic acid** and soluble **arsenates** precipitate *lead arsenate*, white, from neutral or alkaline solutions of lead salts, soluble in the fixed alkali hydroxides and in nitric acid, insoluble in acetic acid. For the composition of the arsenites and arsenates of lead see (*D.*, **2**, 2, 565). Hot potassium stannite ($SnCl_2$ in solution by **KOH**) gives with lead salts or lead hydroxide a black precipitate of metallic lead.

h.—**Chromic acid** and soluble **chromates**—both K_2CrO_4 and $K_2Cr_2O_7$—precipitate *lead chromate*, $PbCrO_4$, yellow, soluble in the fixed alkali hydroxides (distinction from bismuth), insoluble in excess of chromic acid (distinction from barium), insoluble in ammonium hydroxide (distinction from silver), decomposed by moderately concentrated nitric and hydrochloric acids, insoluble in acetic acid. The precipitate is formed as follows:

$$PbCl_2 + K_2Cr_2O_7 + H_2O = PbCrO_4 + H_2CrO_4 + 2KCl.$$

7. Ignition.—Insoluble lead salts may be tested by fusion in a porcelain crucible with sodium carbonate. The lead is converted into lead oxide, **PbO** (*a*). After fusion and digestion with warm water, the aqueous solution is tested for acids, and the residue for bases after dissolving in nitric or acetic acid. If charcoal (or some organic compounds as sugar, tartrates, etc.) be present, metallic lead is formed (*b*); and with excess of charcoal the acid radicle may also be changed (*c*). If the fusion with sodium carbo-

nate is made on a piece of charcoal, instead of in a crucible, using the reducing flame of the blowpipe, globules of metallic lead are produced and at the same time the charcoal is covered with a yellow incrustation of lead oxide, **PbO**.

(*a*) $PbCl_2 + Na_2CO_3 = 2NaCl + PbO + CO_2$
(*b*) $2PbSO_4 + 2Na_2CO_3 + C = 2Pb + 2Na_2SO_4 + 3CO_2$
(*c*) $2PbSO_4 + 2Na_2CO_3 + 5C = 2Pb + 2Na_2S + 7CO_2$

8. **Detection.**—Lead is precipitated, incompletely, from its solutions by **HCl** as $PbCl_2$; separated from **AgCl** and **HgCl** by hot water, and confirmed by H_2S, H_2SO_4, K_2CrO_4, and **KI**. It is separated (in the second group) from **As**, **Sb**, **Sn**, etc., by non-solubility of the sulphide in $(NH_4)_2S_x$; from **HgS** by HNO_3 ; from **Bi**, **Cu**, and **Cd** by precipitation with dilute sulphuric acid. Insoluble compounds are transposed by an alkali sulphide, being then treated as lead in the second group, or they are examined by ignition as described in (7).

9. **Estimation.**—(*a*) As an oxide into which it is converted by ignition (if a carbonate or nitrate), or by precipitation and subsequent ignition. (*b*) As a sulphate. Add to the solution twice its volume of alcohol, precipitate with H_2SO_4, and after washing with alcohol ignite and weigh. (*c*) It is converted into an acetate, or sodium acetate is added to the solution, then precipitated with $K_2Cr_2O_7$, and after drying at 100°, weighed as $PbCrO_4$. (*d*) It is converted into **PbS**, free sulphur added, and after ignition in hydrogen gas weighed as **PbS**. (*e*) The lead is precipitated with standardized sodium iodate and the excess of iodate is determined by retitration. Lead iodate is less soluble in water than lead sulphate (Cameron, *J. C.*, 1879, **36**, 484). (*f*) In presence of bismuth, ignite the halogen compound, or convert into a sulphide and ignite in a current of bromine. The haloid salts of bismuth sublime upon ignition (Steen, *Z. angew.*, 1895, 530). (*g*) *Gas volumetric method.* Precipitate as a chromate, filter, wash and transfer to an azotometer with dilute sulphuric acid and estimate the amount of chromium by the volume of oxygen set free by hydrogen peroxide (Baumann, *Z. angew.*, 1891, 329).

10. **Oxidation.**—Metallic lead precipitates the free metals from solutions of **Hg**, **Ag**, **Au**, **Pt**, **Bi**, and **Cu**. Lead as a dyad is oxidized to the tetrad as stated in (4), also electrolytically in separation from **Cu** (Nissenson, *Z. angew.*, 1893, 646). Pb^{IV} is reduced to **Pb**° in presence of dilute H_2SO_4 by nascent hydrogen, and by all metals capable of producing nascent hydrogen (such as **Al**, **Zn**, **Sn**, **Mg**, **Fe**), and to **Pb**″ by soluble compounds of **Hg**′, **Sn**″, **Sb**‴, **As**‴, (AsH_3 gas), **Cu**′, **Fe**″, **Cr**‴, **Mn**″, **Mn**‴, Mn^{IV}, Mn^{VI}. Also by $H_2C_2O_4$, HNO_2, H_3PO_2, H_3PO_3, **P**, SO_2, H_2S, **HCl**, **HBr**, **HI**, **HCN**, **HCNS**, $H_4Fe(CN)_6$, glycerine, tartaric acid, sugar, urea, and *very many* other organic compounds. In many cases the reduction to **Pb**″ or to **Pb**° takes place in presence of **KOH**. The freshly precipitated peroxide oxidizes ammonia, NH_3, to nitrite and nitrate in the course of a few hours (Pollacci, *Arch. Pharm.*, 1886, **224**, 176).

From lead solutions **Zn**, **Mg**, **Al**, **Co**, and **Cd** precipitate metallic lead.

§58. Mercury (Hydrargyrum) Hg = 200.0. Valence one and two.

1. **Properties.**—*Specific gravity*, liquid, 13.5953 (Volkmann, *W. A.*, 1881, **13**, 209); solid, 14.1932 (Mallet, *Proc. R. Soc.*, 1877, **26**, 71). *Melting (freezing) point*, —38.85° (Mallet, *Phil. Mag.*, 1877, (5), **4**, 145). *Boiling point*, 357.33° at 760 mm. (Ramsay and Young, *J. C.*, 1885, **47**, 657). It is the only metal which is a liquid at ordinary temperatures, white when pure, with a slightly bluish tinge, and having a brilliant silvery lustre. The precipitated or finely divided mercury appears as a dark gray powder. Mercury may be "extinguished" or "deadened," *i. e.*, reduced to the finely divided state, by shaking with sugar, grease, chalk, turpentine, ether, etc. It is slightly volatile even at —13° (Regnault, *C. r.*, 1881, **93**, 308); is not oxidized by air or oxygen at ordinary temperature (Shenstone and Cundall, *J. C.*, 1887, **51**, 619). The solid metal is composed of octahedral and needle-shaped crystals, is very ductile and is easily cut with a knife. Owing to its very strong cohesive property it forms a convex surface with glass, etc. It is a good conductor of electricity, and forms amalgams with **Al**, **Ba**, **Bi**, **Cd**, **Cs**, **Ca**, **Cr**, **Co**, **Cu**, **Au**, **Fe**, **Pb**, **Mg**, **Mn**, **Ni**, **Os**, **Pd**, **Pt**, **K**, **Ag**, **Na**, **Tl**, **Sn**, and **Zn**. Amalgams with special alloys of gold, silver, tin, and zinc are used for filling teeth.

2. **Occurrence.**—Occasionally found native in small globules associated with cinnabar, in the containing gangue, and as amalgam (Ag_2Hg_3 to $Ag_{36}Hg$); the principal mercury mineral is cinnabar, **HgS**. It occurs also as calomel, **HgCl**, generally associated with cinnabar.

Found in Austria, Spain, Peru, China, Russia, California, Texas and Oregon.

3. **Preparation.**—The extraction of mercury from cinnabar, which may be considered as practically the only ore of this metal, is effected: (*a*) by oxidation with a regulated supply of air, and volatilization of the liberated metal, which distils over and is condensed: $HgS + O_2 = Hg + SO_2$; (*b*) by mixing the ore with lime, and distilling: $4HgS + 4CaO = 4Hg + 3CaS + CaSO_4$. (*c*) The ore is heated with iron (smithy scales): **Hg**, **FeS**, and SO_2 are produced. The mercury is usually condensed in a trough of water. Commercial mercury is freed from dirt and other impurities by pressing through leather or by passing through a cone of writing or filter paper having a small pin-hole in the apex. For the separation of mercury from small quantities of **Pb**, **Sn**, **Zn**, and **Ag** without distilling, see Brühl (*B.*, 1879, **12**, 204), Meyer (*B.*, 1879, **12**, 437) and Crafts (*Bl.*, 1888, (2), **49**, 856).

4. **Oxides.**—Mercury forms two oxides, Hg_2O and **HgO**. *Mercurous oxide*, Hg_2O, is a black powder formed by the action of fixed alkalis on mercurous salts. It is converted by gentle heat into **Hg** and **HgO** and by a higher (red) heat, to **Hg** and **O**. *Mercuric oxide*, **HgO**, is made (*1*) by keeping **Hg** at its boiling point for a month or longer in a flask filled with air; (*2*) by heating $HgNO_3$ or $Hg(NO_3)_2$ with about an equal weight of metallic mercury: $Hg(NO_3)_2 + 3Hg = 4HgO + 2NO$; (*3*) by precipitating mercuric salts with **KOH** or **NaOH**. Made by (*1*) and (*2*) it is red, by (*3*) yellow. On heating it changes to vermillion red, then black, and on cooling regains its original color. A red heat decomposes it completely into **Hg** and **O**. Mercury forms no hydroxides.

5. **Solubilities.**—*a.*—*Metal.*—Unaffected by treatment with alkalis. The most effective solvent of mercury is nitric acid. It dissolves readily in the dilute acid hot or cold; with the strong acid, heat is soon generated; and with considerable quantities of material, the action acquires an explosive violence. At ordinary temperatures, nitric acid, when applied in excess, produces normal mercuric nitrate, but when the mercury is in excess, and the acid is cold and dilute, mercurous nitrate is formed; in all cases, chiefly nitric oxide gas is generated. Both mercurous and mercuric nitrates require a little free nitric acid to hold them in solution. This free nitric acid gradually oxidizes mercurous to mercuric, making a clear solution of $Hg(NO_3)_2$, if there is sufficient HNO_3 present, otherwise a basic mercuric nitrate may precipitate. A solution of mercurous nitrate may be kept free from mercuric nitrate by placing some *metallic* mercury in the bottle containing it; still after standing some weeks a basic mercurous nitrate crystallizes out, which a fresh supply of nitric acid will dissolve. Sulphur attacks mercury even in the barometric vacuum, forming **HgS** (Schrotter,

J. C., 1873, **26**, 476). H_2SO_4, concentrated at 25° has no action on **Hg** (Pitman. *J. Am. Soc.*, 1898, **20**, 100). With the hot concentrated acid SO_2 is evolved and Hg_2SO_4 is formed if **Hg** be in great excess; $HgSO_4$ if the H_2SO_4 be in excess. Hydrochloric acid gas at 200° is without action (Berthelot, *A. Ch.*, 1856, (3), **46**, 492); also the acid sp. gr., 1.20. Bailey and Fowler (*J. C.*, 1888, **53**, 759) say that dry hydrochloric acid gas in presence of oxygen and mercury, at ordinary temperature for three weeks, forms Hg_2OCl_2 without evolution of hydrogen: $2Hg + 2HCl + O_2 = Hg_2OCl_2,H_2O$. Hydrobromic and hydriodic acids, gases, both attack mercury, evolve **H**, and form respectively **HgBr** and **HgI** (Berthelot, *l. c.*). Hydrosulphuric acid, dry gas, at 100° does not attack dry **Hg** (Berthelot, *l. c.*). Hydrosulphuric acid, in solution, and alkali sulphides form **HgS**. Chlorine, bromine and iodine, dry or moist, attack the metal; mercurous salts are formed if the mercury be in excess, mercuric salts if the halogen be in excess.

b.—Oxides.—**Mercurous oxide**, Hg_2O, is a black powder insoluble in water or alkalis. Hydrochloric acid forms **HgCl**; sulphuric acid forms Hg_2SO_4, changed by boiling with excess of acid to $HgSO_4$; nitric acid forms $HgNO_3$, changed by excess of acid to $Hg(NO_3)_2$. **Mercuric oxide** is soluble in acids, insoluble in alkalis, soluble in 20,000 to 30,000 parts water (Bineau, *C. r.*, 1855, **41**, 509). It is red when produced by heating in the dry way and orange yellow when formed by precipitation with alkalis. It is decomposed by alkali chlorides forming $HgCl_2$* (Mialhe, *A. Ch.*, 1842, (3), **5**, 177), soluble in NH_4Cl, from which solution NH_4OH produces the white precipitate $NH_2Cl,NHgH_2Cl + NH_2HgCl$ (Ditte, *C. r.*, 1891, **112**, 859), soluble in KI_2 forming $2KI,HgI_2$ (Jehn, *J. C.*, 1872, **25**, 987).

c.—Salts.—Mercury forms two well marked classes of salts—*mercurous*, monovalent, and *mercuric*, divalent—most mercurous compounds are permanent in the air, but are changed by powerful oxidizing agents to mercuric compounds. The latter are somewhat more stable, but are changed by many reducing agents, first to mercurous compounds and then to metallic mercury (10). Solutions of mercury salts redden litmus. Many of the salts of mercury are either insoluble in water, or require the presence of free acid to keep them in solution, being decomposed by water at a certain degree of dilution, precipitating a basic salt and leaving an acid salt in solution. **Mercurous** chloride, bromide, and iodide are insoluble in water; the sulphate is soluble in 500 parts cold and 300 parts hot water, soluble in dilute nitric acid (Wackenroder, *A.*, 1842, **41**, 319). The acetate has about the same solubilities as the sulphate. Mercurous nitrate is completely soluble in water. On standing it gradually changes to mercuric nitrate, prevented by the presence of free mercury, but if free mercury be present a precipitate of basic mercurous nitrate gradually forms. **Mercuric** chloride is soluble in 16 parts of cold water and 3 parts

* The Law of Mass-Action requires that where the constituents of a slightly-ionized substance are present that substance shall form at the expense of those more strongly ionized. Such a slightly-ionized body is $HgCl_2$. When **HgO** is brought into contact with **KCl** solution **Hg** and **Cl** combine to form the non-dissociated $HgCl_2$, leaving **K** and **O**, which unite with water, imparting to the solution a strong alkaline reaction. **KBr** and **KI** act even more strongly. **HgO**, although from the ready decomposition of its salts by water and from its easy reducibility a weak base, yet will replace the alkali metals where a little-dissociated **Hg** compound results.

An excess of $Hg(NO_3)_2$ dissolves chloride, bromide, and iodide of **Hg** and **Ag** owing to the same cause, the **Hg**″ ions of the strongly dissociated nitrate decreasing the already slight dissociation of the mercuric haloids (§ **44**). The failure of $HgCl_2$ to give many of the precipitation-reactions obtainable with other soluble mercuric salts is of course due to the same fact—the slight concentration of **Hg**″ ions (§ **45**).

warm water; the bromide is soluble in 94 parts water at 9° and 4-5 parts at 100°, decomposed by warm nitric or sulphuric acids; the iodide is soluble in about 25,000 parts water (Bourgoin, *A. Ch.*, 1884 (6), **3**, 429), soluble in $Na_2S_2O_3$ (Eder and Ulen, *J. C.*, 1882, **42**, 806), and in many alkali salts, forming double salts. Normal mercuric sulphate is decomposed by water into a soluble acid sulphate and the basic sulphate, $HgSO_4$, $2HgO$, which is practically insoluble (soluble in 43,478 parts water at 16°, Cameron, *Analyst*, 1880, 144). The normal nitrate is *deliquescent*, very soluble in a small amount of water, but more water precipitates the nearly insoluble basic nitrate, $3HgO.N_2O_5$, changed by repeated washing into the oxide, HgO (Millon, *A. Ch.*, 1846 (3), **18**, 361). The basic nitrate is soluble in dilute nitric acid. The cyanide is soluble in eight parts water at 15°. The acetate is readily soluble, the chromate and citrate sparingly, and the sulphide, iodide, iodate, basic carbonate, oxalate, phosphate, arsenate, arsenite, ferrocyanide, and tartrate are insoluble in water.

6. **Reactions.** *a.*—**Fixed alkali hydroxides** precipitate, from solutions of **mercurous salts**, *mercurous oxide*, Hg_2O, black, insoluble in alkalis, readily transposed by acids; from solutions of mercuric salts, the alkali, added short of saturation, precipitates reddish-brown basic salts; when added in excess, the *orange-yellow mercuric oxide*, HgO, is precipitated. If the solution of mercuric salt be strongly acid no precipitate will be obtained owing to the combination of the mercuric salt with the alkali salt formed, producing a double salt in which the mercury is present in the acid ion unaffected by the hydroxyl ion. **Ammonium hydroxide** and **carbonate** precipitate from solutions of mercurous salts, black mixtures of mercury and mercuric ammonium compounds. The same is true of the action of ammonium hydroxide on insoluble mercurous salts: $2HgCl + 2NH_4OH = Hg + NH_2HgCl + 2H_2O + NH_4Cl$; $6HgNO_3 + 6NH_4OH = 3Hg + (NH_2HgNO_3)_2HgO + 4NH_4NO_3 + 5H_2O$; $4Hg_2SO_4 + 8NH_4OH = 4Hg + (HgH_2N)_2SO_4.2HgO + 3(NH_4)_2SO_4 + 6H_2O$; or uniting the salt in different manner, $4HgCl + 4NH_4OH = 2Hg + Hg_2NCl.NH_4Cl + 2NH_4Cl + 4H_2O$. Examination with a microscope reveals the presence of Hg°. The mercuric ammonium precipitate dissolves in a saturated solution of $(NH_4)_2SO_4$ containing ammonium hydroxide and can thus be separated from the **Hg** (Francois, *J. Pharm.*, 1897 (6), **5**, 388; Turi, *Gazzetta*, 1893, **23**, ii, 231; Pesci, *Gazzetta*, 1891, **21**, ii, 569; Barfoed, *J. pr.*, 1889, (2), **39**, 201). With **mercuric salts** ammonium hydroxide produces "white precipitate," recognizable in very dilute solutions; that with cold neutral solutions of mercuric chloride being mercurammonium chloride, $(NH_2Hg)Cl$, also called nitrogen dihydrogen mercuric chloride (*a*); with hot solution and excess of ammonium hydroxide, dimercurammonium chloride, NHg_2Cl, also called nitrogen dimercuric chloride (*b*) is formed. Treat-

ing with fixed alkali hydroxide until no more ammonia is evolved changes the former compound to the latter (Pesci, *l. c.*). The precipitates are easily soluble in hydrochloric acid, slightly soluble in strong ammonium hydroxide, and more or less soluble in ammonium salts, especially ammonium **nitrate and carbonate** (Johnson, *C. N.*, 1889, **59**, 234). A soluble combination of ammonium chloride with mercuric chloride, $2NH_4Cl.HgCl_2$, or ammonium mercuric chloride, called "sal alembroth," is not precipitated by ammonium hydroxide, but potassium hydroxide precipitates therefrom the white mercurammonium chloride, $(NH_3)_2HgCl_2$ (*c*):

(*a*) $HgCl_2 + 2NH_4OH = NH_2HgCl + NH_4Cl + 2H_2O$
(*b*) $2HgCl_2 + 4NH_4OH = NHg_2Cl + 3NH_4Cl + 4H_2O$
(*c*) $2NH_4Cl.HgCl_2 + 2KOH = (NH_3)_2HgCl_2 + 2KCl + 2H_2O$

A solution of $HgCl_2$ in **KI** with an excess of **KOH** (Nessler's Reagent) is precipitated by NH_4OH (or by ammonium salts), as NHg_2I (§207, 6*k*).

Fixed alkali carbonates precipitate from mercurous salts an unstable *mercurous carbonate*, Hg_2CO_3, gray, blackening to basic carbonate and oxide when heated. Carbonates of barium, strontium, calcium and magnesium precipitate mercurous carbonate in the cold. Mercuric salts are precipitated as *red-brown basic salts*, which, by excess of the reagent with heat, are converted into the yellow mercuric oxide. The basic salt formed with mercuric chloride is an oxychloride, $HgCl_2.(HgO)_2$, $_3$, or $_4$; with mercuric nitrate, a basic carbonate, $(HgO)_3HgCO_3$. Barium carbonate precipitates a basic salt in the cold, from the nitrate, but not from the chloride.

b.—**Oxalic acid** and soluble **oxalates** precipitate from solutions of mercurous salts *mercurous oxalate*, $Hg_2C_2O_4$, white, slightly soluble in nitric acid; from solutions of mercuric salts, except $HgCl_2$, *mercuric oxalate*, HgC_2O_4, white, easily soluble in hydrochloric acid, difficultly soluble in nitric acid. A solution of $HgCl_2$ boiled in the sunlight with $(NH_4)_2C_2O_4$ gives **HgCl** and CO_2.

Hydrocyanic acid and alkali **cyanides** decompose mercurous salts into metallic mercury, a gray precipitate, and mercuric cyanide, which remains in solution. Mercuric salts are not precipitated, since the cyanide is readily soluble in water. Soluble **ferrocyanides** form with mercurous salts a white gelatinous precipitate, soon turning bluish green; with mercuric salts a white precipitate, soon turning blue. Soluble **ferricyanides** form with mercurous salts a yellowish green precipitate; with mercuric salts a green precipitate, soluble, in hydrochloric acid. **Potassium thiocyanate** precipitates mercurous thiocyanate, **HgCNS**, white, from solutions of mercurous salts (Claus, *J. pr.*, 1838, **15**, 406); from solutions of mercuric salts, mercuric thiocyanate, $Hg(CNS)_2$, white, soluble in hot water (Philipp, *Z Ch.*, 1867, 553).

c.—Nitric acid never acts as a precipitant of mercury salts, the salts being more soluble in strong nitric acid than in water or the dilute acid; also nitric acid dissolves all insoluble salts of mercury except **HgS**, which is insoluble in the hot acid (*sp. gr.* 1.42) (Howe, *Am.*, 1887, **8**, 75). **HgCl** is slowly dissolved by nitric acid on boiling. All mercurous salts are oxidized to mercuric salts by excess of nitric acid.

d.—**Hypophosphorous acid** reduces mercuric salts to **Hg°**, but the presence of hydrogen peroxide causes the formation of **HgCl** from $HgCl_2$ and is of value as a quantitative method for estimation of mercury (Vanino and Treubert, *B.*, 1897, **30**, 1999). **Phosphorus acid** also reduces $HgCl_2$ to **HgCl**.

Phosphoric acid and alkali **phosphates** precipitate, from mercurous salts, *mercurous phosphate*, Hg_3PO_4, white, if the reagent be in excess; but if $HgNO_3$ be in excess, $Hg_3PO_4.HgNO_3$, white, with a yellowish tinge. Mercurous phosphate is soluble in dilute HNO_3, insoluble in H_3PO_4. From mercuric nitrate, *mercuric phosphate*, $Hg_3(PO_4)_2$, white, is precipitated, soluble in HNO_3, **HCl**,

and ammonium salts, insoluble in H_3PO_4. Phosphoric acid does not precipitate $HgCl_2$, and Na_2HPO_4 does not precipitate the white $Hg_3(PO_4)_2$ from $HgCl_2$, but on standing a portion of the mercury separates as a dark brown precipitate (Haack, *J. C.*, 1891, **60**, 400; 1892, **62**, 530).

e.—**Hydrosulphuric acid** and soluble **sulphides**, precipitate from **mercurous** salts, *mercuric sulphide*, **HgS**, black, and *mercury*, gray. Mercurous sulphide, Hg_2S, does not exist at ordinary temperatures. According to Antony and Sestini (*Gazzetta*, 1894, **24**, i, 193), it is formed at —10° by the action of H_2S on **HgCl**, decomposing at 0° into **HgS** and **Hg**. From **mercuric** salts there is formed, first, a white precipitate, soluble in acids and excess of the mercuric salts, on further additions of the reagent, the precipitate becomes yellow-orange, then brown, and finally black. This progressive variation of color is **characteristic** of mercury. The final and stable black precipitate is mercuric sulphide, **HgS**; the lighter colored precipitates consist of unions of the original mercuric salt with mercuric sulphide, as $HgCl_2.HgS$, the proportion of **HgS** being greater with the darker precipitates. When sublimed and triturated, the black mercuric sulphide is converted to the red (vermillion), without chemical change. Mercuric sulphide is insoluble in dilute HNO_3 (distinction from all other metallic sulphides); insoluble in **HCl** (Field, *J. C.*, 1860, **12**, 158); soluble in chlorine (nitro-hydrochloric acid); insoluble in $(NH_4)_2S$ except when **KOH** or **NaOH** be present (Volhard, *A.*, 1891, **255**, 252); soluble in K_2S (Ditte, *C. r.*, 1884, **98**, 1271), more readily if **KOH** be present (separation from **Pb**, **Ag**, **Bi**, and **Cu**) (Polstorff and Bülow, *Arch. Pharm.*, 1891, **229**, 292). A little **HgS** (0.5–1.0 mg.) may dissolve in ammonium polysulphide when a large amount of mercury is present (A. A. Noyes, *J., Am. Chem. Soc.*, **29**, 170). It is soluble in K_2CS_3 (one part **S**, two parts CS_2, and 23 parts **KOH**, *sp. gr.* 1.13) (separation from **Pb**, **Cu**, and **Bi**); reprecipitated as sulphide by **HCl** (Rosenbladt, *Z.*, 1887, **26**, 15).

Mercurous nitrate forms with sodium thiosulphate a grayish black precipitate, part of the mercury remaining in solution. Mercurous chloride forms metallic mercury and some mercury salt in solution as double salt (Schnauss, *J. C.*, 1876, **29**, 342). Mercuric chloride added to sodium thiosulphate forms a white precipitate, which blackens on standing; if the mercuric chloride be added in excess a bright yellow precipitate is formed, which blackens when boiled with water, nitric acid or sulphuric acid, but does not dissolve or blacken on boiling with hydrochloric acid. Sodium thiosulphate added to mercuric chloride forms a white precipitate, which blackens on standing or on adding excess of thiosulphate, but if excess of thiosulphate be rapidly added to $HgCl_2$ no precipitate is formed; boiling or long standing produces the black precipitate. Mercuric salts are not completely precipitated by sodium thiosulphate. The black precipitate is **HgS**.

Sulphurous acid and soluble **sulphites** form from mercurous solutions a black precipitate of complex sulphite (Divers and Shimidzu, *J. C.*, 1886, **49**, 567). Mercuric nitrate with sulphurous acid forms slowly a flocculent white precipitate soluble in nitric acid. The precipitate and solution contain mercurosum as evidenced by **HCl**. Mercuric nitrate with soluble sulphites forms a voluminous white precipitate, soluble in HNO_3 and containing mercurosum. Mercuric chloride is not precipitated by sulphurous acid or sulphites in the cold, but is reduced, by boiling with sulphurous acid, to **HgCl** and then to **Hg**°

Sulphuric acid and soluble **sulphates** precipitate from mercurous solutions not too dilute, *mercurous sulphate*, Hg_2SO_4, white, decomposed by boiling water, sparingly soluble in cold water (*5c*), soluble in nitric acid and blackened by alkalis. Mercuric salts are not precipitated by sulphuric acid or sulphates. For action of H_2SO_4 on $HgCl_2$ see next paragraph and (§269, 8, footnote).

f.—**Hydrochloric acid** and soluble **chlorides** precipitate from solutions of mercurous salts, *mercurous chloride*, **HgCl**, "Calomel," white, insoluble in water, slowly soluble in hot concentrated **HCl**. Boiling nitric acid slowly dissolves it, forming $Hg(NO_3)_2$ and $HgCl_2$; dissolved by chlorine or nitrohydrochloric acid to $HgCl_2$; soluble in $Hg(NO_3)_2$ (*5b* footnote) (Dreschsel, *J. C.*, 1882, **42**, 18). This precipitation of mercurous salts by hydrochloric acid is a sharp separation from mercuric salts and places mercurous mercury in the First (Silver) Group of Metals. Mercuric salts are not precipitated by hydrochloric acid or soluble chlorides, unless the mercuric solution is more concentrated than possible for a mercuric chloride solution under the same conditions, *i. e.*, a strong solution of $Hg(NO_3)_2$ gives a precipitate of $HgCl_2$ on addition of **HCl**, soluble on addition of water. Mercuric chloride is not decomposed by sulphuric acid. A compound $HgCl_2.H_2SO_4$ is formed which sublimes undecomposed. The same compound is formed when $HgSO_4$ is treated with **HCl** and distilled (Ditte, *A. Ch.*, 1879, (5), **17**, 120).

Hydrobromic acid and soluble **bromides** precipitate, from solutions of mercurous salts, *mercurous bromide*, **HgBr**, yellowish white, insoluble in water, alcohol, and dilute nitric acid; from concentrated solutions of mercuric salts, *mercuric bromide*, $HgBr_2$, white, decomposed by concentrated nitric acid. Mercuric bromide is soluble in excess of mercuric salts (*5b* footnote), or in excess of the precipitant; hence, unless added in suitable proportions, no precipitate will be produced. Sulphuric acid does not transpose $HgBr_2$ but forms compounds exactly analogous to those with $HgCl_2$. Excess of concentrated H_2SO_4 gives some **Br** with $HgBr_2$.

Hydriodic acid and soluble **iodides** precipitate from solutions of mercurous salts, *mercurous iodide*, **HgI**, greenish yellow—"the green iodide of mercury"—nearly insoluble in water, insoluble in alcohol (distinction from mercuric iodide), soluble in mercurous and mercuric nitrates; decomposed by soluble iodides with formation of **Hg** and HgI_2, the latter being dissolved as a double salt with the soluble iodide: $2HgI + 2KI = Hg + HgI_2.2KI$. Mercurous chloride is transposed by **HI** or **KI** to form **HgI**, excess of the reagent reacts according to the above equation (D., **2**, 2, 867). Ammonium hydroxide in the cold decomposes **HgI** into **Hg** and HgI_2 (Francois, *J. Pharm.*, 1897, (6), **5**, 388).

Mercuric salts are precipitated as *mercuric iodide*, HgI_2, first reddish-

yellow then red, soluble in 24,814 parts of water at 17.5° (Bourgoin, *A. Ch.*, 1884, (6), **3**, 429), soluble in concentrated nitric and hydrochloric acids; quickly soluble in solutions of the iodides of all the more positive metals, *i. e.* in excess of its precipitant, by formation of soluble double iodides; as $(KI)_2HgI_2$ variable to $KIHgI_2$. A hot concentrated solution of potassium iodide dissolves $3HgI_2$ for every $2KI$. The first crystals from this solution are $KIHgI_2$. These are decomposed by pure water, and require a little alkali iodide for perfect solution, but they are soluble in alcohol and ether. A solution of dipotassium mercuric tetraiodide, $K_2HgI_4 = (KI)_2HgI_2$ (sometimes designated the iodo-hydrargyrate of potassium), is precipitated by ammonium hydroxide as mercurammonium iodide, NHg_2I (Nessler's test), and by the alkaloids (Mayer's reagent).

Potassium bromate precipitates, from solutions of mercurous nitrate, mercurous bromate, $HgBrO_3$, white, soluble in excess of mercurous nitrate and in nitric acid; from solutions of mercuric nitrate, mercuric bromate, $Hg(BrO_3)_2$, white, soluble in nitric acid, hydrochloric acid, and in excess of mercuric nitrate, in 650 parts of cold and 64 parts of hot water (Rammelsberg, *Pogg.*, 1842, **55**, 79). No precipitate is formed when potassium bromate is added to mercuric chloride (5*b*, footnote). **Iodic acid** and soluble **iodates** precipitate solutions of mercurous salts as *mercurous iodate*, $HgIO_3$, white with yellowish tint, soluble with difficulty in dilute nitric acid, readily soluble in HCl by oxidation to mercuric salt. Mercuric nitrate is precipitated as *mercuric iodate*, $Hg(IO_3)_2$, white, soluble in HCl, insoluble in HNO_3 and H_2SO_4, soluble in NH_4Cl, transposed and then dissolved by KI. Mercuric chloride is not precipitated by KIO_3 (5*b*, footnote) (Cameron, *C. N.*, 1876, **33**, 253).

g.—**Arsenous acid** or **arsenites** form a white precipitate with mercurous nitrate, soluble in HNO_3 (Simon, *Pogg.*, 1837, **40**, 442). Mercuric nitrate is precipitated by a solution of arsenous acid; the precipitate is soluble in HNO_3 (*D.*, **2**, 2, 920). **Arsenic acid** or Na_2HAsO_4 precipitates from mercurous nitrate $3Hg_2AsO_4.HgNO_3.H_2O$, light yellow if the $HgNO_3$ be in excess (*D.*, **2**, 2, 921); dark red Hg_3AsO_4 if the arsenate be in excess. Hg_3AsO_4 is changed by cold HCl to $HgCl$ and H_3AsO_4, by boiling with HCl to Hg^0, $HgCl_2$, and H_3AsO_4; and is soluble unchanged in cold HNO_3, insoluble in water and acetic acid (Simon, *Pogg.*, 1837, **41**, 424). **Arsenic acid** and soluble **arsenates** precipitate from mercuric nitrate, $Hg_3(AsO_4)_2$, white, soluble in HNO_3 and HCl, slightly soluble in water. Arsenic acid and potassium arsenate do not precipitate mercuric chloride from its solutions.

Stannous chloride precipitates solutions of mercuric salts (by reduction), as mercurous chloride, white; or if the stannous chloride be in excess, as metallic mercury, gray to black (a valuable final test for mercuric salts) (10).

h.—Soluble **chromates** precipitate from mercurous solutions *mercurous chromate*, Hg_2CrO_4, brick-red, insoluble in water, readily transposed by HCl to $HgCl$ and H_2CrO_4, soluble with difficulty in HNO_3 without oxidation (Richter, *B.*, 1882, **15**, 1489). Mercuric nitrate is precipitated by soluble chromates as a light yellow precipitate, rapidly turning dark brown, easily soluble in dilute acids and in $HgCl_2$. Mercuric chloride forms a precipitate with normal chromates, but not with $K_2Cr_2O_7$.

7. **Ignition.**—Mercury from all its compounds is volatilized by heat as the undecomposed salt or as the free metal. Mercurous chloride (Debray,

J. C., 1877, **31**, 47) and bromide and mercuric chloride and iodide sublime (in glass tubes) *undecomposed*—the sublimate condensing (in the cold part of the tube) without change. Most other compounds of mercury are decomposed by vaporization, and give a sublimate of metallic mercury (mixed with sulphur, if from the sulphide, etc.). *All* compounds of mercury, dry and intimately mixed with dry **sodium carbonate**, and heated in a glass tube closed at one end, give a sublimate of metallic mercury as a gray mirror coat on the inner surface of the cold part of the tube. Under the magnifier, the coating is seen to consist of globules, and by gently rubbing with a glass rod or a wire, globules visible to the unaided eye are obtained.

8. **Detection.**—Mercury in the *mercurous* condition belongs to the FIRST GROUP (silver group), and is completely precipitated by **HCl**. It is identified by the action of ammonium hydroxide, changing the white precipitate of mercurous chloride to the black precipitate of metallic mercury and nitrogen dihydrogen mercuric chloride (a delicate and characteristic test for **Hg′**). Mercury in the *mercuric* condition belongs to the SECOND GROUP (tin and copper group), and is separated from all other metals of that group by the non-solubility of the sulphide in $(NH_4)_2S_x$ and in dilute HNO_3. The sulphide is dissolved in nitrohydrochloric acid, and the presence of mercury confirmed by the precipitation of **Hg°** on a copper wire, or by the reduction to **HgCl** or **Hg°** by $SnCl_2$.

9. **Estimation.**—(*a*) As metallic mercury. The mercury is reduced by means of **CaO** in a combustion-tube at a red heat in a current of CO_2. The sublimed mercury is condensed in a flask of water, and, after decanting the water, dried in a bell-jar over sulphuric acid without application of heat. The mercury may also be reduced from its solution by $SnCl_2$ (or H_3PO_3 at 100°) and dried as above. (*b*) As mercurous chloride. It is first reduced to **Hg′** by H_3PO_3 (Uslar, *Z.*, 1895, **34**, 391), which must not be heated above 60°, otherwise metallic mercury will be formed; and after precipitation by **HCl** and drying on a weighed filter at 100°, it is weighed as **HgCl**. Or enough **HCl** is added to combine with the mercury, then the **Hg″** is reduced to **Hg′** by $FeSO_4$ in presence of **NaOH**: $2HgO + 2FeO + 3H_2O = Hg_2O + 2Fe(OH)_3$. H_2SO_4 is added, which causes the formation of **HgCl**, which is dried on a weighed filter at 100°. (*c*) As **HgS**. It is precipitated by H_2S, and weighed in same manner as the chloride. Any free sulphur mixed with the precipitate should be removed by CS_2. (*d*) As **HgO**, by heating the nitrate in a bulb-tube in a current of dry air not hot enough to decompose the **HgO**. (*e*) Volumetrically, by $Na_2S_2O_3$; from the *nitrate* the precipitate is *yellow*, from the *chloride* it is *white*:

$$3Hg(NO_3)_2 + 2Na_2S_2O_3 + 2H_2O = Hg_3S_2(NO_3)_2 + 2Na_2SO_4 + 4HNO_3$$
$$3HgCl_2 + 2Na_2S_2O_3 + 2H_2O = Hg_3S_2Cl_2 + 2Na_2SO_4 + 4HCl.$$

(*f*) Volumetrically, $HgCl_2$ is reduced to Hg_2O by $FeSO_4$ in presence of **KOH**, and after acidulating with H_2SO_4 the excess of $FeSO_4$ is determined by $K_2Cr_2O_7$ or $KMnO_4$ (Jüptner, *C. C.*, 1882, 727). (*g*) By iodine. It is converted into **HgCl** and then dissolved in a graduated solution of **I** dissolved in **KI**: $2HgCl + 6KI + I_2 = 2K_2HgI_4 + 2KCl$. The excess of iodine is determined by $Na_2S_2O_3$. (*h*) The measured solution of $HgCl_2$ is added to a graduated solution of **KI**: $4KI + HgCl_2 = K_2HgI_4 + 2KCl$. The instant the amount of $HgCl_2$ shown in the equation is exceeded a red precipitate of HgI_2 appears. (*i*) *Volumetric*,

by adding a few drops of ammonium hydroxide to $HgCl_2$ and then titrating with standard **KCN**, the ammonium hydroxide precipitate disappears when the mercury becomes $Hg(CN)_2$ (Hannay, *J. C.*, 1873, **26**, 570; Tuson, *J. C.*, 1877, **32**, 679). (*j*) *Electrolytically*, by obtaining the mercury as $HgNO_3$, $Hg(NO_3)_2$, or Hg_2SO_4 and precipitating as Hg° on platinum by the electric current. Mercuric chloride cannot be used, as it is partly reduced to **HgCl**, and that is not readily reduced to Hg° by the electric current (Hannay, *l. c.*).

10. **Oxidation.**—Free mercury (Hg°) precipitates **Ag**, **Au**, and **Pt** from their solutions, and reduces mercuric salts to mercurous salts (Hada, *J. C.*, 1896, **69**, 1667). Potassium permanganate in the cold oxidizes the metal to Hg_2O, when hot to **HgO** (Kirchmann, *J. C.*, 1873, **26**, 476). Mercury and mercurous salts are oxidized to mercuric salts by **Br**, **Cl**, **I**, HNO_3, H_2SO_4 (concentrated and hot), and $HClO_3$.

Reducing agents, as **Pb**, **Sn**, **Sn″**, **Bi**, **Cu**, **Cu′**, **Cd**, **Al**, **Fe**, **Co**, **Zn**, **Th**[1], **Mg**, H_3PO_2, H_3PO_3 and H_2SO_3, precipitate, from the solutions of mercuric and mercurous nitrates, *dark-gray* Hg°; from solution of mercuric chloride, or in presence of chlorides, *first the white*, **HgCl**, *then gray* Hg°. Strong acidulation with nitric acid interferes with the reduction, and heating promotes it.

The reducing agent most frequently employed is stannous chloride:

$$2HgCl_2 + SnCl_2 = 2HgCl + SnCl_4$$
$$2HgCl + SnCl_2 = 2Hg + SnCl_4$$

or
$$HgCl_2 + SnCl_2 = Hg + SnCl_4$$

also
$$2Hg(NO_3)_2 + SnCl_2 = 2HgCl + Sn(NO_3)_4$$

A clean strip of copper, placed in a slightly acid solution of a salt of mercury, becomes coated with metallic mercury, and when gently rubbed with cloth or paper presents the tin-white lustre of the metal, the coating being driven off by heat; $2HgNO_3 + Cu = 2Hg + Cu(NO_3)_2$. Formic acid reduces mercuric to mercurous chloride, and in the cold does not affect further reduction. Dry mercuric chloride, moistened with alcohol, is reduced by metallic iron, a bright strip of which is corroded soon after immersion into the powder tested (a delicate distinction from mercurous chloride).

§59. Silver (Argentum) Ag = 107.88. Monovalent.

1. **Properties.**—*Specific gravity* 10.512 heated in vacuo (Dumas, *C. N.*, 1878, **37**, 82). *Melting point*, 960.7° (Heycock and Neville, *J. C.*, 1895, **67**, 1024). Does not appreciably vaporize at 1567° (V. and C. Meyer, *B.*, 1879, **12**, 1428). It is the whitest of metals, harder than gold and softer than copper. Silver is hardened by copper; United States silver coin contains 90 per cent silver and 10 per cent copper. In malleability and ductility it is inferior only to gold; and as a conductor of heat and electricity it exceeds all other metals.

2. **Occurrence.**—Found in a free state in United States, Mexico, Peru, Siberia, etc.; alone, and with gold as a component of other minerals, *e. g.*, galena, pyrite, chalcopyrite, and many other ores. The most important silver minerals are

[1]Reid, *C. N.*, 1865, **12**, 242; [2]Heumann, *J. C.*, 1875, **28**, 132.

argentite, Ag_2S, stephanite, Ag_5SbS_4, pyrargyrite, Ag_3SbS_3, proustite, Ag_3AsS_3, cerargyrite, **AgCl**.

3. **Preparation.**—(*a*) Argentiferous ores are smelted with lead ores, coke and limestone in a blast furnace; silver (and gold) alloys with the reduced lead, and is subsequently separated from it by Parkes' or Betts' process. (*b*) It is amalgamated with mercury and the mercury separated by distillation. (*c*) It is brought into solution and the metal precipitated by copper. (*d*) It is very easily reduced from the oxide or carbonate by heat alone, and from all its compounds by ignition with hydrogen, carbon, carbon monoxide and organic compounds.

4. **Oxides.**—*Silver oxide*, Ag_2O, argentic oxide, is formed by the action of alkali hydroxides on silver salts or by heating the carbonate to 200°. It is a brown powder, a strong oxidizing agent, decomposed at 300° into metallic silver and oxygen. Concerning the existence of argentous oxide, Ag_4O, and silver peroxide, Ag_2O_2, and their properties, see Muthmann (*B.*, 1887, **20**, 983); Pfordten (*B.*, 1887, **20**, 1458) and Bailey (*C. N.*, 1887, **55**, 263).

5. **Solubilities.**—*a.—Metal.*—The *fixed alkalis* do not act upon silver, hence silver crucibles are used instead of platinum for fusion with caustic alkalis. Ammonium hydroxide dissolves finely divided silver, no action if air be excluded. Acetic acid is without action (Lea, *Am. S.*, 1892, **144**, 444). Nitric acid is the ordinary solvent for silver, the 50 per cent acid being most effective, while the dilute acid free from nitrous acid has little or no action (Lea, *l. c.*); silver nitrate is formed, nitrogen peroxide being the chief product of the reduction of the nitric acid (Higley and Davis, *Am.*, 1897, **18**, 587). Silver is not oxidized by water or air at any temperature; it is attacked by phosphorus or by substances easily liberating phosphorus; it is tarnished in contact with hydrosulphuric acid, soluble sulphides, and many organic compounds containing sulphur; except that pure *dry* hydrosulphuric acid is without action upon pure dry silver (Cabell, *C. N.*, 1884, **50**, 208). Dilute sulphuric acid slowly dissolves finely divided silver (Lea, *l. c.*), a sulphate being formed while, with the hot concentrated acid, sulphur dioxide is evolved. Hydrochloric acid, sp. gr., 1.20, is without action upon pure silver, but the metal is readily attacked by chlorine, bromine or iodine. *b.—Oxide.*—**Silver oxide**, Ag_2O, soluble in 3000 parts of water, combines with nearly all acids, except CO_2, forming the corresponding salts. The hydroxide is not known.

c.—Salts.—Silver forms a greater number of insoluble salts than any other known metal, though in this respect mercury and lead are quite similar. The nitrate is very soluble in water, 100 parts water dissolving 227.3 parts at 19.5°, soluble in glycerol, and sparingly soluble in alcohol and ether. The chlorate dissolves in about ten parts cold water; the acetate in 100 parts; the sulphate in about 200 parts cold water and 88 parts at 100°, and is more soluble in nitric or sulphuric acid than in water; the borate, thiosulphate, and citrate are sparingly soluble in water. The oxalate, tartrate, carbonate, cyanide, ferrocyanide, ferricyanide, phosphate, sulphide, sulphite, chloride, bromide, iodide, iodate, arsenite, arsenate, and chromate are insoluble in water.

The chloride is soluble in 244 parts **HCl**, but its solubility is very much lessened by the presence of mercurous chloride (Ruyssen and Varenne, *Bl.*, 1881, **36**, 5). If a solution of silver nitrate be dropped into concentrated hydrochloric acid no precipitate appears until one half per cent of the **HCl** becomes **AgCl** (Pierre, *J. C.*, 1872, **25**, 123). Concentrated nitric acid upon long continued boiling scarcely attacks **AgCl** (Thorpe, *J. C.*, 1872, **25**, 453); sulphuric acid, *sp. gr.* 1.84, completely transposes even the fused

chloride on long boiling (Sauer, *J. C.*, 1874, **27**, 335). Silver chloride is also soluble in ammonium hydroxide and carbonate; in sodium chloride forming a double salt; in a concentrated solution of mercuric nitrate (§68, 1; §58, 5*b* footnote); and in many other metallic chlorides and alkali salts to a greater or less extent. All the salts of silver which are insoluble in water are soluble in ammonium hydroxide, except the sulphide and iodide; in ammonium carbonate, except the bromide, iodide, and sulphide, the bromide very slightly soluble; in cold dilute nitric acid, except the chloride, bromide, bromate, iodide, iodate, cyanide, and thiocyanate; in a solution of potassium cyanide (and by many other cyanides) except the sulphide; and in alkali thiosulphates almost without exception.

6. **Reactions.** *a.*—The **fixed alkali hydroxides** precipitate from solutions of silver salts (in absence of citrates), *silver oxide*, Ag_2O, grayish brown, insoluble in excess of the reagents; soluble in acids, alkali cyanides, and thiosulphates; somewhat soluble in ammonium salts. Most silver salts are transposed on boiling with the fixed alkalis, except the iodide, which is not thus transposed (Vogel, *J. C.*, 1871, **24**, 313).

Ammonium hydroxide, in neutral solutions of silver salts, forms the same precipitate, Ag_2O, very easily dissolving in excess, by formation of silver ammonium hydroxide, NH_3AgOH : $AgNO_3 + 2NH_4OH = NH_3AgOH + NH_4NO_3 + H_2O$ (Prescott, *J. Am. Soc.*, 1880, **2**, 32). In solutions containing much free acid, all precipitation is prevented by the ammonium salt formed with the formation of silver ammonium nitrate, NH_3AgNO_3 or in the presence of excess of ammonia as $(NH_3)_2AgNO_3$.

Alkali carbonates precipitate silver carbonate, Ag_2CO_3, white or yellowish white, very slightly soluble in water and in the fixed alkali carbonates, readily soluble in ammonium hydroxide and carbonate, transposed by inorganic acids forming the corresponding salts. Carbon dioxide does not transpose silver salts.

b.—**Oxalic acid** and soluble **oxalates** precipitate *silver oxalate*, $Ag_2C_2O_4$, white, slightly soluble in water, soluble with difficulty in dilute nitric or sulphuric acids, readily soluble in ammonium hydroxide. When heated it decomposes with detonation, forming metallic silver.

Potassium cyanide precipitates from neutral or slightly acid solutions *silver cyanide*, **AgCN**, white, quickly soluble in excess of the reagent as silver potassium cyanide, **AgCN.KCN**. Hydrocyanic acid precipitates solutions of silver salts but the precipitate does not dissolve in excess of the reagent. Silver cyanide is transposed by H_2SO_4 or **HCl** and is soluble in ammonium hydroxide and carbonate (Schneider, *J. pr.*, 1868, **104**, 83). The ready solubility of nearly all silver compounds in potassium cyanide (5*c*) affords a means of separating silver from many minerals.

Potassium ferrocyanide precipitates *silver ferrocyanide*, $Ag_4Fe(CN)_6$, yellowish white, soluble with difficulty in ammonium hydroxide and carbonate;

metallic silver separates on boiling and a ferricyanide is formed. The ferrocyanide is not decomposed by hydrochloric acid, but it is changed to the ferricyanide by nitric acid. Exposure to the air gives it a blue tinge. **Potassium ferricyanide** precipitates *silver ferricyanide*, $Ag_3Fe(CN)_6$, reddish yellow, readily soluble in ammonium hydroxide and carbonate. **Potassium thiocyanate** gives *silver thiocyanate*, **AgCNS**, white, soluble in ammonium hydroxide and carbonate, insoluble in dilute acids. Concentrated sulphuric acid with the aid of heat dissolves silver thiocyanate when some free silver nitrate is present. This may be used as a separation from silver chloride, which is transposed by hot concentrated sulphuric acid only on long-continued boiling (5*c*). To effect this separation a little silver nitrate should be added to the silver precipitates and then concentrated sulphuric acid and heat. To avoid danger of decomposition of the chloride the mixture should not be heated above 200°. The pure silver thiocyanate (silver nitrate being absent) is decomposed by hot concentrated sulphuric acid with formation of a black precipitate containing silver.

c.—**Silver nitrate** is soluble in 500 parts of concentrated nitric acid (Schultz, *Z. Ch.*, 1869, 531), and is precipitated from its concentrated water solutions by the addition of **concentrated nitric acid.** *d.*—**Disodium phosphate** precipitates *silver phosphate*, Ag_3PO_4, yellow, soluble in dilute nitric acid, in phosphoric acid, and in ammonium hydroxide and carbonate; but little soluble in dilute acetic acid. **Sodium pyrophosphate** precipitates *silver pyrophosphate*, white, same solubilities as the orthophosphate.

e.—**Hydrosulphuric acid** and **soluble sulphides** precipitate from neutral, acid or alkaline solutions *silver sulphide*, Ag_2S, black, soluble in moderately strong nitric acid (distinction from mercury), slightly soluble in potassium cyanide (distinction from copper), insoluble in alkali sulphides (distinction from arsenic, antimony, and tin). Certain insoluble sulphides form silver sulphide from solutions of silver nitrate,* *e. g.*, cupric sulphide gives silver sulphide, cuprous sulphide gives silver sulphide and metallic silver, in both cases cupric nitrate resulting (Schneider, *J. C.*, 1875, **28**, 133 and 612).

Thiosulphates precipitate silver thiosulphate, $Ag_2S_2O_3$, white, unstable, readily soluble in excess of the precipitant, by formation of double thiosulpahtes; with excess of sodium thiosulphate $Na_4Ag_2(S_2O_3)_3$ is formed (Cohen, *J. C.*, 1896, **70**, ii, 167). Silver thiosulphate turns black on standing or heating; $Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4$. **Sulphurous acid** and soluble **sulphites** precipitate *silver sulphite*, Ag_2SO_3, white, readily soluble in excess of alkali sulphite or in dilute nitric acid; on boiling precipitated as metallic silver with formation of sulphuric acid. **Sulphuric acid** and soluble *sulphates* precipitate silver sulphate, Ag_2SO_4, white, from concentrated solutions of the nitrate or chlorate; sparingly soluble in water, quite soluble in concentrated sulphuric acid.

f.—**Hydrochloric acid** and soluble **chlorides** precipitate *silver chloride*, **AgCl**, white, curdy; separated on shaking the solution; turning violet to brown on exposure to the light; fusible without decomposition; very easily soluble in ammonium hydroxide as *ammonio silver chloride*, $(NH_3)_3(AgCl)_2$ (Jarry, *C. r.*, 1897, **124**, 288), according to the following equation:

$$2AgCl + 3NH_4OH = 3NH_3.2AgCl + 3H_2O.$$

On acidifying the solution with nitric acid the silver chloride is reprecipitated as follows:

$$3NH_3.2AgCl + 3HNO_3 = 2AgCl + 3NH_4NO_3.$$

If mercurous chloride be present with silver chloride the solubility in ammonium hydroxide is greatly lessened, in fact a great excess of mercurous

* Ag_2S is one of the least soluble of the sulphides. See § 57, 6c, footnote.

chloride may entirely prevent the solution of silver chloride in ammonium hydroxide by forming metallic silver. $AgCl + 3HgCl + 4NH_4OH = Ag + 2Hg + 2NH_2HgCl + 2NH_4Cl + 4H_2O$. Silver chloride is quite soluble in a solution of mercuric nitrate, which, if present in large excess, may entirely prevent the precipitation of the silver chloride by hydrochloric acid. The precipitation by hydrochloric acid (in absence of a great excess of $Hg(NO_3)_2$) is the most delicate of the ordinary tests for silver, being recognized in 250,000 parts of water. As mercuric salts are not at all precipitated by **HCl** and lead salts only imperfectly, silver is the only metal which belongs exclusively to the FIRST OR SILVER GROUP OF BASES (§16).

Hydrobromic acid and soluble *bromides* precipitate *silver bromide*, **AgBr**, white, with a slight yellowish tint; but slightly soluble in excess of alkali bromides, and much less easily soluble in ammonium hydroxide than silver chloride. If silver nitrate be added to a bromide containing an excess of ammonium hydroxide, the precipitate which first forms readily dissolves on shaking; no solution is obtained with the iodide.

Hydriodic acid and soluble **iodides** precipitate *silver iodide*, **AgI**, pale yellow, soluble in excess of the concentrated reagents by formation of double iodides, as **KIAgI**, which are decomposed by dilution with much water. The precipitate dissolves in 26,000 parts of ten per cent ammonium hydroxide; not at all in a five per cent solution (Longi, *Gazzetta*, 1883, **13**, 87). It is insoluble in dilute acids, but is decomposed by hot concentrated nitric or sulphuric acids.

Silver bromate formed by adding **potassium bromate** to silver nitrate is soluble in about 600 parts water and in 320.4 parts nitric acid (*sp. gr.*, 1.21) at 25°, and readily soluble in ammonium hydroxide. *Silver iodate* formed in manner similar to the bromate is soluble in about 28,000 parts water and in 1044.3 parts nitric acid (*sp. gr.*, 1.21) at 25°, and readily soluble in ammonium hydroxide (Longi, *l. c.*).

g.—Soluble **arsenites** precipitate *silver arsenite*, Ag_3AsO_3, yellow, very readily soluble in dilute acids and in ammonium hydroxide. Soluble **arsenates** precipitate *silver arsenate*, Ag_3AsO_4, red-brown, soluble in ammonium hydroxide, nitric acid, arsenic acid, and almost insoluble in acetic acid.

A solution of **alkali stannite**—as K_2SnO_2—precipitates *metallic silver* from solutions of silver salts. A solution of silver nitrate in a great excess of ammonium hydroxide constitutes a very delicate reagent to detect the presence of tin in the stannous condition in the presence of fixed alkalis; antimony does not interfere if a great excess of ammonium hydroxide be present.

h.—**Chromates** and **dichromates**, as K_2CrO_4 and $K_2Cr_2O_7$, precipitate *silver chromate*, Ag_2CrO_4, dull-red, sparingly soluble in water and in dilute nitric acid, soluble in ammonium hydroxide.

7. **Ignition.**—Silver nitrate melts undecomposed at 218°, at a red heat it is decomposed into **Ag°**, **O**, **N**, and **NO** (Fischer, *Pogg.*, 1848, **74**, 120). Silver chloride fuses at 451°, the bromide at 427°, and the iodide at 527°. On charcoal with sodium carbonate, silver is reduced from all its compounds by the blow-pipe, attested by a bright malleable globule. Lead and zinc, and elements more volatile, may be separated from silver by their gradual volatilization under the blow-pipe, or in the assay furnace (see Cupellation in works on the assay of the precious metals).

8. **Detection.**—Silver is identified by its precipitation with hydrochloric acid, the insolubility of the precipitate in hot water, and its solubility in ammonium hydroxide, with reprecipitation on rendering acid with nitric acid (§61).

9. **Estimation.**—(*a*) As metallic silver, into which it is converted by direct ignition if it is the oxide or carbonate, or by ignition in hydrogen if the chloride, bromide, iodide or sulphide (Vogel, *J. C.*, 1871, **24**, 1009). (*b*) It is precipitated as **AgCl**, and after igniting to incipient fusion, weighed. (*c*) It is converted into Ag_2S by H_2S, and weighed after drying at 100°; inadmissible in case of an acid that might liberate free sulphur. (*d*) Add **KCN** until a solution of $KAg(CN)_2$ is formed, precipitate with HNO_3, and after drying at 100°, weigh as **AgCN**. (*e*) Volumetrically, by adding a graduated solution of **NaCl** until a precipitate is no longer formed. This may be varied by adding the measured silver solution to the graduated **NaCl** solution, containing a few drops of K_2CrO_4, until the red precipitate begins to form. (*f*) Volumetrically, add a graduated solution of ammonium thiocyanate, containing ferric sulphate, until the red color ceases to disappear. (*g*) Add the measured silver solution to a standard solution of **KCN** until a permanent white precipitate is formed.

10. **Oxidation.**—Metallic silver precipitates gold and platinum from their solutions, reduces cupric chloride to cuprous chloride,[1] mercuric chloride to mercurous chloride, and permanganates to manganese dioxide[2]. Silver is precipitated from its solutions by: **Pb**, **PbS**[3], **Hg**, **As**[4], AsH_3, **Sb**, SbH_3, **Sn**, **Sn″**, **Bi**, **Cu**, **Cu′**, **Cd**, **Te**, **Fe**, **FeS**[4], **Al**, **Mn**, **Zn**, **Mg**, **P**[4], PH_3, $H_4P_2O_6$, H_2SO_3, SiH_4[5], H_2O_2[6], and **H** (very slowly)[7].

In alkaline mixture silver is also reduced by **Hg′**, **As‴**, **Sb‴**, **Bi‴**, and **Mn″**. An amalgam of mercury and tin reduces insoluble compounds of silver in the wet way, the silver amalgamates with the mercury and the tin becomes Sn^{IV} (Laur, *C. r.*, 1882, **95**, 38).

Ferrous sulphate in the cold incompletely reduces silver salts; on boiling, the ferric salt formed is reduced and the silver dissolved (Lea, *l. c.*). In the gradual reduction of silver by certain organic reagents, the metal is obtained as a bright silver coating or mirror upon the inner surface of the test tube or other glass vessel. Usually a slightly ammoniacal solution of silver nitrate is used and allowed to stand some time with the reagent; such as alcoholic solution of oil of cloves or cassia, formic acid, aldehyde, chloral, tartaric acid, etc. Gentle warming facilitates the result. If a good mirror is desired, great care must be taken to free the inner surface of the glass from all organic impurities by careful washing with ether, chloroform, etc. In these deoxidations, generally the nitric acid radical of the silver nitrate is not decomposed, but nitric acid is left: $4AgNO_3 + 2H_2O = 4Ag + 4HNO_3 + O_2$.

Light acts upon nearly all salts of silver when mixed with gelatine or other organic substances used in preparing photographic plates, etc. These plates contain various silver salts, frequently the bromide or iodide, or both together. The nature of the chemical change is not fully understood. It has been shown, however, that silver chloride on exposure to the light loses chlorine, and there is considerable evidence to prove that when the silver halides are acted upon by light, a subhalide such as Ag_2Cl, Ag_2Br or Ag_2I is formed. When the plate which has been exposed to light is treated with a reducing agent, the reduction of the silver is carried to the metallic state, the black silver producing the image. The nitrate in crystal or pure water solution, the phosphate, bromide,

[1] Lea, *Am. S.*, 1892, **144**, 444. [2] *D.*, **2**, 2, 759. [3] Skey, *C. N.*, 1871, **23**, 232. [4] Senderens, *C. r.*, 1887, **104**, 175. [5] D., **2**, 1, 456. [6] Riegler, *J. C.*, 1896, **70**, ii, 471. [7] Pellet, *B.*, 1874, **7**, 656; Schwarzenbach and Kritschewsky, *Z.*, 1886, **25**, 374; Cooke, *C. N.*, 1888, **58**, 103. [8] Millon, *Am. S.*, 1863, **86**, 417.

§60. Comparison of Certain Reactions of First-Group (Silver Group) Metals.

Taken in Solution of their Nitrates or Acetates.

	Pb	Ag	Hg′	Hg″
KOH or **NaOH**, in excess	Solution (§57, 6*a*).	Ag_2O, grayish brown (§59, 6*a*).	Hg_2O, black (§58, 6*a*).	**HgO**, yellow (§58, 6*a*).
NH_4OH, in excess	White precipitate, basic salt, not formed in the acetate (§57, 6*a*).	Solution (§59, 6*a*).	**Hg** and NH_2HgNO_3, black (§58, 6*a*).	NHg_2NO_3 or NH_2HgCl, white (§58, 6*a*).
Chlorides	$PbCl_2$, white, sparingly soluble in cold water, more readily if hot; insoluble in NH_4OH (§57, 6*f*).	**AgCl**, white, insoluble in water, soluble in NH_4OH (§59, 6*f*).	**HgCl**, white, insoluble in water, decomposed by NH_4OH (§58, 6*f*).	.....
Bromides	$PbBr_2$, less soluble in water than $PbCl_2$, insoluble in NH_4OH (§57, 6*f*).	**AgBr**, yellowish white, soluble in NH_4OH (§59, 6*f*).	**HgBr**, yellowish white, decomposed by NH_4OH (§58, 6*f*).	$HgBr_2$, white, fairly soluble in water, or in the Hg″ salt or the bromide (§58, 6*f*)
Iodides	PbI_2, orange-yellow, sparingly soluble in the alkali iodides (§57, 6*f*).	**AgI**, pale yellow, soluble in the alkali iodides (§59, 6*f*).	**HgI**, yellowish green, decomposed by the alkali iodides (§58, 6*f*).	HgI_2, red, readily soluble in the alkali iodides (§58, 6*f*).
Sulphates	$PbSO_4$, white, almost insoluble in water (§57, 6*e*).	Ag_2SO_4, white, if solution be not too dilute (§59, 5*c*).	Hg_2SO_4, white, if solution be not too dilute (§58, 5*c*).	.....
Chromates	$PbCrO_4$, yellow, soluble in **KOH** (§57, 6*h*).	Ag_2CrO_4, purple red, soluble in NH_4OH (§59, 6*h*).	Hg_2CrO_4, orange yellow (§58, 6*h*).	Basic salt, yellow to reddish yellow (§58, 6*h*).
Zinc	Pb (§57, 10).	**Ag** (§59, 10).	**Hg** (§58, 10).	Hg′ and then **Hg** (§58, 10).
Lead	.....	**Ag** (§59, 10).	**Hg** (§58, 10).	Hg′ and then **Hg** (§57, 10).
Mercury	.....	**Ag** (§59, 10).	.....	.....
Stannous Salts	.....	**Ag** (§59, 6*g*).	**Hg** (§58, 6*g*).	Hg′ and then **Hg** (§58, 6*g*).

§61. TABLE FOR ANALYSIS OF THE SILVER GROUP (FIRST GROUP). See §312.

The precipitate is washed on the filter with one or two small portions of cold water (§62); then treated with hot water and filtered (§64).

Residue:* $AgCl$, $HgCl$.

Digest with **ammonium hydroxide,** *and filter.*

Residue: Hg° and **NH_2HgCl**, *black* (§58, 6*a*).

[Lead oxychloride, *white* (§57, 6*a*).]

The black color is evidence of mercury, and that it was present in the mercurous condition. Dissolve in a little **HCl**, to which a few drops of conc. **HNO_3** have been added. Boil out excess of chlorine and test solution with a copper wire and stannous chloride

For the further examination of the black precipitate, see §58, 6*a*.

Study the table at §60.

Read §66 and §67.

Solution: $3NH_3.2AgCl$.

Boil to expel the excess of ammonium hydroxide and acidify with **nitric acid.** A white curdy precipitate is **AgCl.** If solution is very acid nearly neutralize with ammonia and add a few drops of **KCn** solution. **HgCl** will dissolve.

If the **NH_4OH** solution is turbid, due to the formation of a basic lead chloride (§57, 6*a*), filter, and then treat as above.

The original material (evaporated to dryness, if a solution) may be tested by the blow-pipe on charcoal (§59, 7); giving metallic silver, which may be dissolved in nitric acid (§59, 5*a*) and the resulting solution examined by the usual tests for silver.

Read §66 and §68.

Solution: $PbCl_2$ (§64).

Divide the solution into four portions, and test with the following:

(1) **H_2SO_4**, giving **$PbSO_4$**, white (§57, 6*e*).
(2) **H_2S**, " **PbS**, black (§57, 6*e*).
(3) **K_2CrO_4**, " **$PbCrO_4$**, yellow (§57, 6*h*).
(4) **KI** †, " **PbI_2**, yellow (§57, 6*f*).

If an abundance of lead chloride be present, the hot-water solution will deposit the needle crystals of the chloride as the solution cools (§57, 5*c*).

Any of the precipitates may be tested by the blow-pipe (§57, 7).

Read §64 and §65.

* If lead is found, wash with small portions of hot water and test for lead until precipitate is free from this metal.

† In precipitating the lead chloride with potassium iodide avoid an excess of the reagent and dissolve the precipitate in hot water, obtaining the golden yellow scales of **PbI_2** on cooling.

iodide and cyanide are not decomposed by light alone; but light greatly hastens their decomposition by organic substances, or other reducing agents, as of solution of silver nitrate in rain water, or written as an ink upon fabrics. Silver is the base of most *indelible inks*.

DIRECTIONS FOR THE ANALYSIS OF THE METALS OF THE FIRST GROUP.

§62. **Manipulation.**—To the solution acid with nitric acid add hydrochloric acid (whenever directions call for the addition of a reagent it is to be used reagent strength unless otherwise stated) drop by drop (§32) until no further precipitate is formed and the solution is distinctly acid to litmus (§36). The precipitate will consist of the chlorides of **Pb**, **Hg′**, and **Ag**. Shake thoroughly and allow to stand a few moments before filtering; if the solution is warm it should be cooled to the temperature of the room. Decant the solution and precipitate upon a filter paper previously wetted (§35) with water and wash two or three times with cold water or until the filtrate is not strongly acid to litmus. The washings with cold water should be added to the first filtrate and the whole marked and set aside to be tested for the metals of the remaining groups (§16).

§63. *Notes.*—1. Failure to obtain a precipitate upon the addition of **HCl** to an acid reaction is proof of the absence of **Hg′** and **Ag′**, but a solution of a lead salt may be present, of such a degree of dilution that the lead chloride formed will be soluble in the dilute acid (§57, 5c).

2. The solution should not be strongly acid with nitric acid, as it forms nitrohydrochloric acid with the hydrochloric acid, causing oxidation of the **Hg′** (§58, 5c). Lead chloride is also more soluble in nitric acid than in dilute hydrochloric acid (§57, 5c). By a study of the solubilities of the silver group metals it will be seen that H_2SO_4, **HCl**, **HBr** or **HI** cannot be used in preparing a solution for analysis when these metals are present.

3. A great excess of acid is to be avoided, as it may interfere with the reaction in Group II. (§57, 6e). Complete precipitation should be assured by testing the filtrate with a drop of **HCl**, when no further precipitation should occur (§32). If a white precipitate is formed by adding a drop of **HCl** to the filtrate it is evident that the precipitation was not complete and more **HCl** should be added and the group separation repeated (§11).

4. The presence of a slight excess of *dilute* acid does not aid or hinder the precipitation of the **Hg′** or **Ag′**, but as $PbCl_2$ is less soluble in dilute **HCl** than in water, a moderate excess of the acid causes a more complete precipitation of that metal in the first group.

5. *Concentrated* **HCl** dissolves the chlorides of the first group quite appreciably (§59, 5c).

6. Hydrochloric acid added to certain solutions may cause a precipitate when none of the first group metals are present. Some of the more important conditions are mentioned. It will be noted that a number of these are alkaline solutions and will give precipitates with other acids than **HCl**. It is advisable in these cases to acidify with HNO_3 before adding **HCl** in order to avoid error from this source.

a. A concentrated solution of $BaCl_2$ is precipitated without change by the addition of **HCl**, readily soluble in water (§186, 5c).

b. An acid solution of **Sb**, **Bi**, or **Sn**, with some other acid than **HCl**, and saturated with water as far as possible without precipitation, on the addition of **HCl**, precipitates the oxychloride of the corresponding metal (§76, 6f). These precipitates are readily soluble in an excess of the **HCl**. It must, however, be remembered that a trace of **AgCl** will also be dissolved by an excess of **HCl** (§59, 5c).

c. Solutions of metallic oxides in the alkali hydroxides are precipitated when neutralized with acids, *e. g.*, $K_2ZnO_2 + 2HCl = Zn(OH)_2 + 2KCl$.

d. The sulphides of **As**, **Sb**, **Sn**, **Au**, **Pt**, **Mo** (**Ir**, **W**, **Ge**, **V**, **Se** and **Te**) in solution with the alkali polysulphides are reprecipitated together with sulphur on the addition of **HCl** (§69, 6e).

e. Soluble polysulphides and thiosulphates give a precipitate of sulphur, white, with **HCl** (§256, 3a).

f. Certain soluble double cyanides, as $Ni(CN)_2.2KCN$, are precipitated as insoluble cyanides, $Ni(CN)_2$, on the addition of **HCl** (§133, 6b).

g. Solutions of silicates (§249, 4), borates, tungstates, molybdates; also benzoates, salicylates, urates, and certain other organic salts, are precipitated by acidulation with **HCl**, many of the precipitates being soluble on further addition of the acid.

h. Acidulation with **HCl** may induce changes of oxidation or reduction, which in certain mixtures may result in precipitation: for example, **Cu″** salts with **KCNS** in ammoniacal solution (§77, 6b); mixture of solutions of **KI** and KIO_3 (§280, 6, *B*, 7), etc.

7. If the precipitate, obtained by the addition of **HCl** to the solution, is colored or does not give further reactions which are conclusive and perfectly satisfactory in every respect, it should be separated by filtration, and treated as a solid substance taken for examination (see conversion of solids into liquids, §301).

8. Compounds of the first group metals insoluble in water or acids are transposed to sulphides by digestion with an alkali sulphide. The lead and silver sulphides thus formed are readily soluble in hot dilute nitric acid. The mercurous compounds are changed to mercuric sulphide (§58, 5a and 6c), a second group mercury compound insoluble in HNO_3.

9. If but one metal of the first group be present, the action of NH_4OH determines which it is; $PbCl_2$ does not change color or dissolve; **HgCl** blackens; and **AgCl** dissolves (§60).

§64. **Manipulation.**—The precipitate (white) on the filter should now be washed once or twice with hot water. The first hot water should be poured upon the precipitate a second time. This hot filtrate is divided into four portions and each portion tested separately for lead with the following reagents, H_2SO_4, H_2S, $K_2Cr_2O_7$, and **KI** (§57, 6 *c*, *h*, and *f*) giving white, black, and yellow precipitates:

The yellow precipitate with potassium iodide (the **KI** must not be used in great excess (§57, 5c)) should be allowed to settle, the liquid decanted, and the precipitate redissolved in hot water, to a colorless solution which upon cooling deposits beautiful yellow crystalline scales of PbI_2 (characteristic of lead).

§65. *Notes.*—1. Lead is never completely precipitated in the first group (§57, 6f). The presence of a moderate excess of dilute **HCl** and the cooling of the solution both favor the precipitation.

2. Lead can be completely separated from the second group metals by sulphuric acid applied to the original solution (§57, 6c, §95 and §98), but that would necessitate a regrouping of the metals; as, **Ba**, **Sr**, and **Ca** would also be precipitated (Zettnow, *Z.*, 1867, **6**, 438).

3. In order to precipitate the lead chloride, not removed in the first group, in the second group with H_2S, the solutions must not be strongly acid, either the excess of **HCl** should be removed by evaporation or the solution should be diluted (§57, 6c, and §81, 3, 5 and 9).

4. If the lead chloride is not all washed out with hot water it is changed to an insoluble basic salt (white) by the NH_4OH, part remaining on the filter and part carried through mechanically which causes turbidity to the am-

monium hydroxide solution of the **AgCl** and makes necessary the filtration of that solution before the addition of HNO_3, otherwise it does not interfere.

5. The precipitation of lead as the sulphide while not characteristic of lead, is exceedingly delicate, much more so than the formation of the white $PbSO_4$ (§57, 5*c*). In extremely dilute solutions no precipitate occurs, merely a brown coloration to the solution. The presence of free acid lessens the delicacy of the test.

6. $PbCrO_4$ is blackened by alkali sulphides and dissolved by the fixed alkalis (important distinction from $BaCrO_4$); the solubility in the fixed alkalis is also an important distinction from bismuth chromate (§76, 6*h*).

7. Other tests for lead by reduction on charcoal before the blow-pipe, or in the wet way by **Zn**, should not be omitted (§57, 7 and 10). If to a solution of lead salt nearly neutral a strip of zinc be added, the lead will soon be deposited on the zinc as a spongy mass.

§66. **Manipulation.**—The white precipitate remaining on the filter after washing with hot water consists of **HgCl** and **AgCl**, and some $PbCl_2$ if it has not been well washed. To this precipitate NH_4OH, one or two cc. is added and allowed to pass through the filter into a clean test-tube. An instantaneous blackening of the precipitate is evidence of the presence of mercurous mercury.

The **AgCl** is dissolved by the NH_4OH, and is found in the filtrate; its presence being confirmed by its reprecipitation on rendering the solution acid with HNO_3.

§67. *Notes.*—**Mercury.**—1. The black precipitate on the filter, caused by the addition of NH_4OH to the **HgCl** may be examined under the microscope for the detection of globules of **Hg**°, or the precipitate may be digested with concentrated solution of $(NH_4)_2SO_4$, which dissolves the NH_2HgCl, leaving the **Hg**° unattacked (§58, 6*a*).

2. If the original solution contains no interfering metals, the distinctive reactions of mercurous salts with iodides, chromates and phosphates should be obtained (§58, 6*e*, *h* and *d*).

3. Mercury has but few soluble mercurous compounds, and in preparing solutions of the insoluble compounds for analysis, oxidizing agents are usually employed and the mercury is then found entirely in the second group as a sulphide (§96 and §97).

4. Additional proof may be obtained by mixing a portion of the black residue with sodium carbonate, drying and heating in a glass tube (read §58, 7, also §97, 7).

§68. **Silver.**—1. The presence of a large excess of $Hg(NO_3)_2$ prevents the precipitation of **AgCl** from solutions of silver salts by **HCl** (§59, 5*c*). In this case the metals should be precipitated by H_2S and the well-washed precipitate digested with hot dilute HNO_3. The silver is dissolved as $AgNO_3$, while the mercury is unattacked: $6Ag_2S + 16HNO_3 = 12AgNO_3 + 3S_2 + 4NO + 8H_2O$. After evaporation of the excess of HNO_3 the solution may be treated with **HCl** as an original solution.

2. A small amount of **AgCl** with a large amount of **HgCl** is not dissolved by NH_4OH, but is reduced to **Ag**° by the **Hg**° formed by the addition of the NH_4OH to the **HgCl** (§58, 6*a*, §59, 6*f*, 10 and §60).

3. If **Hg**′ be present and **Ag** is not detected, the black precipitate on the filter should be digested for some time with $(NH_4)_2S$, washed, and boiled with hot dilute nitric acid. The **Ag**, if any be present, is dissolved and separated from the **HgS**:

$$NH_2HgCl + (NH_4)_2S + 2H_2O = HgS + NH_4Cl + 2NH_4OH$$

$$Hg + (NH_4)_2S_x = HgS + (NH_4)_2S_{x-1}$$

The silver may also be detected by treating the precipitate of **HgCl** and **AgCl** with an acid oxidizing agent such as **HCl** and $KClO_3$. The **HgCl** will be oxidized to $HgCl_2$ and dissolved while the **AgCl** remains undissolved.

The silver may also be detected as follows: Boil the original solution with $K_2S_2O_4$ until the **Hg**′ is oxidized to **Hg**″ then add one drop of $MnSO_4$ and more $K_2S_2O_4$ and boil, if the manganese is oxidized to $HMnO_4$ it proves that silver is present.

4. If only a trace of silver be present, its detection by adding HNO_3 to the NH_4OH solution of the chloride may fail, unless the excess of the NH_4OH be first removed by evaporation (because of the solubility of the **AgCl** in the ammonium salt, §**59**, 5*c*).

5. As a further test for silver, the chloride, precipitated by the nitric acid, may be reduced to the metal by zinc: by adding to the ammoniacal solution a few drops of potassium stannite (§**71**, 6*a* and 8); by warming with grape sugar in alkaline mixture. In all cases the well-washed grayish black metal may be dissolved in nitric acid as $AgNO_3$.

6. To identify the acid of silver salts which are insoluble in HNO_3 (**AgCl**, **AgBr**, **AgI**), (*1*) Add metallic zinc and a drop of H_2SO_4; when the silver is all reduced test for the acid in the filtrate. (*2*) Fuse with Na_2CO_3, add water, and test the filtrate for acids. (*3*) Add H_2S, or an alkali sulphide, digest warm for a few minutes, filter and test filtrate for acids. (*4*) Boil with **KOH** or **NaOH** (free from **HCl**), and test the filtrate in the same manner. It must not be overlooked that by the first three methods, and not by the last, bromates and iodates are reduced to bromides and iodides (§**257**, 6*B*).

The Tin and Copper Group (Second Group).

Arsenic, Antimony, Tin, Gold, Platinum, Molybdenum, Mercury, Lead, Bismuth, Copper, Cadmium (Ruthenium, Rhodium, Palladium, Iridium, Osmium, Tungsten, Vanadium, Germanium, Tellurium, Selenium).

The Tin Group (Second Group, Division A).

Arsenic, Antimony, Tin, Gold, Platinum, Molybdenum (Iridium, Tungsten, Vanadium, Germanium, Selenium, Tellurium).

§69. Arsenic. As = 74.96. Valence three and five.

1. **Properties.**—*Specific gravity*, pure crystalline 5.727 at 14°; amorphous 4.716 (Bettendorff, *A.*, 1867, **144**, 110). *Melting point*, 500° (Burgess, Wash. Acad. of Sc., 1–18); between the melting point of antimony and silver (Mallet, *C. N.*, 1872, **26**, 97). *Volatilizes* in an atmosphere of coal gas without melting at 450° (Conechy, *C. N.* 1880 **41**, 189). *Vapor density* (**H** = 1), 147.2 (Deville and Froost *C. r.*, 1863, **56**, 891); therefore the molecule is assumed to contain four atoms (As_4). At a white heat the vapor density is less, but the dissociation is not low enough to indicate As_2 (Mensching and V. Meyer, *B.*, 1887, **20**, 1833). Arsenic exists in two forms, crystalline and amorphous. The crystalline arsenic is steel-gray with a metallic luster, brittle and easily pulverizable; forms beautiful rhombic crystals on sublimation with slow condensation. For ductility, malleability, etc., see D., **2**, 1, 161. Amorphous arsenic is grayish black, of less specific gravity than the crystalline; long heating changes it to the crystalline form (Engel, *C. r.*, 1883, **96**, 1314). The vapor of arsenic is citron-yellow (Le Roux, *C. r.*, 1860, **51**, 171), with an oppressive and poisonous alliaceous odor. It is slowly oxidized in moist (not in dry) air at ordinary temperature; when heated in the air, it burns with a bluish flame and becomes the white arsenous anhydride, As_2O_3. The burning metal evolves a strong garlic odor, not noticed when the pure arsenous anhydride is sublimed. In its physical properties arsenic is a metal, but its failure to act as a base with oxyacids classes it chemically with the non-metallic elements (Adie, *J. C.*, 1889, **55**, 157; Stavenhagen, *Z. angew.*, 1893, 283). Its chief use as a metal is in mixing with lead for making shot.

2. **Occurrence.**—Arsenic is very widely distributed geographically. It is occasionally found native; the chief arsenic minerals are realgar, AsS, and orpiment, As_2S_3; it is an essential constituent of many other minerals, *e. g.*, niccolite, $NiAs$; cobaltite, $CoAsS$; smaltite, $(Co,Ni)As_2$; arsenopyrite, $FeAsS$; löllingite, $FeAs_2$; proustite, Ag_3AsS_3; enargite, Cu_3AsS_4; erythrite, $Co_3(AsO_4)_2 8H_2O$, and many others. Many sulphide ores of zinc and iron contain arsenic, hence arsenic is frequently found in these metals and in sulphuric acid made from the sulphur, and also in the products made therefrom.

3. **Preparation.**—(1) Reduced from its oxide by ignition with carbon; $2As_2O_3 + 3C = As_4 + 3CO_2$. (2) From arsenopyrite, $FeAsS$, by simple ignition, air being excluded; $4FeAsS = 4FeS + As_4$. (3) From orpiment, As_2S_3, by fusion with sodium carbonate and potassium cyanide; $2As_2S_3 + 6Na_2CO_3 + 6KCN = As_4 + 6Na_2S + 6KCNO + 6CO_2$.

4. **Oxides.**—Arsenic forms two oxides: arsenous oxide or anhydride, As_2O_3 (Biltz, *Z. phys. Ch.*, 1896, **19**, 385; *C. C.*, 1896, 793), and arsenic oxide or anhydride, As_2O_5. **Arsenous oxide**, As_2O_3 (*white arsenic, arsenous anhydride, arsenous acid, arsenic trioxide*), is usually prepared by burning arsenic; it may also be prepared by heating arsenic in sulphuric acid till SO_2 is evolved, or by decomposing $AsCl_3$ with H_2O. It sublimes easily on gradually heating, forming beautiful octahedral and tetrahedral crystals. On suddenly heating under pressure it melts, and on cooling forms the opaque arsenic glass. It is very poisonous, usually producing violent vomiting. One hundred fifty milligrams are considered a fatal dose for an adult. No acids (hydroxides) of arsenous anhydride (oxide) have been isolated; but it reacts with bases, forming salts, arsenites, as if derived from the meta, ortho, and pyro arsenous acids. The alkali arsenites are usually meta compounds; the arsenites of the alkaline earths and heavy metals are usually ortho compounds (D., **2**, 1, 170).

Arsenic pentoxide, As_2O_5 (*arsenic anhydride, arsenic oxide*), is formed by heating arsenic acid, H_3AsO_4 (Berzelius, *A. Ch.*, 1819, **11**, 225). It is a white amorphous mass, melts at a dull red heat, is slowly *deliquescent*, combining with water to form H_3AsO_4. The pentoxide, As_2O_5, forms three acids or hydroxides: meta-arsenic acid, $HAsO_3 = AsO_2(OH)$; ortho-arsenic acid, $H_3AsO_4 = AsO(OH)_3$; and pyro-arsenic acid, $H_4As_2O_7 = As_2O_3(OH)_4$; each of these forming a distinct class of arsenates with bases. Ortho-arsenic acid is formed by adding water to arsenic anhydride, $As_2O_5 + 3H_2O = 2H_3AsO_4$, or by oxidizing arsenic or arsenous anhydride with nitric acid. Pyro-arsenic acid is formed by heating the ortho acid to between 140° and 180°: $2H_3AsO_4 = H_4As_2O_7 + H_2O$. The meta acid is formed by heating the ortho or pyro acid to 206°: $H_3AsO_4 = HAsO_3 + H_2O$ (D., *l. c.*).

5. **Solubilities.**—*a.—Metal.*—Arsenic is insoluble in pure water. It is readily attacked by dry chlorine and bromine upon contact and by iodine with the aid of heat. Arsenous chloride, bromide and iodide are formed. It combines with sulphur, forming from As_2S_2 to As_2S_5, depending upon the proportion of sulphur present (Gelis, *A. Ch.*, 1873, (4), **30**, 114). Chlorine and bromine in presence of water oxidize it, first to arsenous then to arsenic acid (Millon, *A. Ch.*, 1842, (3), **6**, 101): $As_4 + 10Cl_2 + 16H_2O = 4H_3AsO_4 + 20HCl$. It is not attacked by concentrated hydrochloric acid at ordinary temperature and but slowly by the hot acid in presence of air forming As_2O_3, then $AsCl_3$; nitric acid readily oxidizes it first to As_2O_3 then to H_3AsO_4; upon fusion with KNO_3 it becomes K_3AsO_4; readily soluble as H_3AsO_4 by nitrohydrochloric acid; sulphuric acid, dilute and cold, is without action; with heat and the more concentrated acid As_2O_3 is formed and the sulphuric acid is reduced to SO_2. Ammonium hydroxide is without action (Guenez, *C. r.*, 1892, **114**, 1186). Hot solution of potassium or sodium hydroxide dissolves it as arsenite: $As_4 + 4KOH + 4H_2O = 4KAsO_2 + 6H_2$.

b.—Oxides.—Arsenous oxide exists in two forms, crystalline and amorphous, the solubilities of which differ considerably (§27). At ordinary temperature 100 parts of water dissolve 3.7 parts of the amorphous and 1.7 parts of the crystalline, several hours being necessary to effect the solution. 100 parts of boiling water dissolve 11.46 parts of the amorphous and 10.14 parts of the crystalline oxide in three hours (Winkler, *J. pr.*, 1885, (2), **31**, 247). The presence of acids greatly increases the solubility in water (Schultz-Sellac, *B.*, 1871, **4**, 109). Arsenous oxide is readily soluble in alkali hydroxides or carbonates to arsenites

(Clayton, *C. N.*, 1891, **64**, 27). *Arsenic pentoxide*, As_2O_5, is *deliquescent*, soluble in water forming H_3AsO_4. The meta and pyro acids are easily soluble in water forming the ortho acid (Kopp, *A. Ch.*, 1856, (3), **48**, 106).

c.—Salts.—Arsenic does not act as a base with oxyacids, but its oxides combine with the metallic oxides to form two classes of salts, **arsenites** and **arsenates**. *Arsenites* of the alkalis are soluble in water, all others are insoluble or only partially so; all are easily soluble in acids. Alkali *arsenates*, and acid arsenates of the alkaline earths, are soluble in water; all are soluble in mineral acids, including H_3AsO_4 (LeFevre, *C. r.*, 1889, **108**, 1058). See also under the respective metals.

Arsenous sulphide, As_2S_3, is insoluble in water when prepared in the dry way; when prepared in the moist way it may be transformed into the soluble colloidal * form by treatment with pure water, from which solutions it is precipitated by solutions of most inorganic salts or acids (Schulze, *J. pr.*, 1882 (2), **25**, 431). The presence of acids or solutions of salts prevents the solubility of As_2S_3 in water. Boiling water slowly decomposes the sulphide forming As_2O_3 and H_2S (Field, *C. N.*, 1861, **3**, 115; Wand. *Arch. Phar.*, 1873, **203**, 296). It is completely decomposed by gaseous **HCl** forming $AsCl_3$ (Piloty and Stock, *B.*, 1897, **30**, 1649), very slightly decomposed and the arsenic dissolved by hot concentrated acid (Field, *l. c.*). Chlorine water and nitric acid decompose it readily with formation of H_3AsO_4; with sulphuric acid As_2O_3 and SO_2 are formed (Rose, *Pogg.*, 1837, **42**, 536). The alkali hydroxides or carbonates dissolve it readily with formation of $RAsO_2$ and $RAsS_2$ ($R = K$, **Na** and NH_4) *D.*, **2**, 1, 183); soluble in alkali sulphides and poly-sulphides forming R_3AsS_3, and $RAsS_2$ (Berzelius, *Pogg.*, 1826, **7**, 137; Nilsson, *J. C.*, 1872, **25**, 599). Whether the ortho, meta or pyro salt is formed, depends upon the amount of alkali sulphide present

Arsenic sulphide, As_2S_5, is insoluble in water; soluble in **HCl** gas, as $AsCl_3$; insoluble in dilute **HCl**, soluble in HNO_3 or chlorine water, as H_3AsO_4; soluble in alkali hydroxides and carbonates, as R_3AsS_4 and R_3AsO_3S: $As_2S_5 + 6NH_4OH = (NH_4)_3AsS_4 + (NH_4)_3AsO_3S + 3H_2O$ (McCay, *Ch. Z.*, 1891, **15**, 476); soluble in alkali sulphides, as R_3AsS_4 (Nilsson, *J. pr.*, 1876 (2), **14**, 171).

Arsenous chloride, bromide and iodide ($AsCl_3$, $AsBr_3$, AsI_3) are decomposed by small amounts of water into the corresponding oxyhalogen compounds, **AsOCl**, etc. A further addition of water decomposes these compounds into arsenous oxide and the halogen acids.

6. **Reactions.**—*a.*—The **alkali hydroxides** and **carbonates** unite with *arsenous* and *arsenic oxides* (acids), the latter with evolution of carbon dioxide, forming soluble alkali *arsenites* and *arsenates*. These alkali salts are chiefly meta arsenites and ortho arsenates (Bloxam, *J. C.*, 1862, **15**, 281; Graham, *Pogg.*, 1834, **32**, 47).

* Colloids is a name given by Graham to a class of glue-like bodies in distinction to the crystalloids, which have a well defined solid form. The colloids are indefinitely soluble in water, giving the little-understood "pseudo solutions," which stand midway between the mechanical suspension or emulsion and the true solution. Gelatine, starch, the metallic sulphides, silicic acid, and the hydroxides of iron and aluminum are some of the substances that may take on the colloid form. The colloid solutions are as a rule broken up by addition of an acid or a neutral salt.

b.—**Oxalic acid** does not reduce arsenic acid* (Naylor and Braithwaite, *Pharm. J. Trans.*, 1883, (3), **13**, 464). **Potassium ferricyanide** in alkaline solution oxidizes arsenous compounds to arsenic compounds, very rapidly when gently warmed. *c.* **Nitric acid** readily oxidizes all other compounds of arsenic to arsenic acid. *d.* **Hypophosphites** in presence of concentrated hydrochloric acid reduce all oxycompounds of arsenic to the metallic state. 0.00001 gram of arsenic may be detected by boiling with 10 cc. strong hydrochloric acid and 0.2 gram calcium hypophosphite (Engel and Bernard, *C. r.*, 1896, **122**, 390; Thiele and Loof, *C. C.*, 1890, 1, 877 and 1078; and Hager, *J. C.*, 1874, **27**, 868).

e.—**Hydrosulphuric** acid precipitates the lemon-yellow *arsenous sulphide*, As_2S_3, from acidulated solutions of arsenous acid. The precipitate forms in presence of concentrated hydrochloric acid. Citric acid and other organic compounds hinder the formation of the precipitate, but do not wholly prevent it if strong hydrochloric acid be present. Nitric acid should not be present in strong excess as it decomposes hydrosulphuric acid, with precipitation of sulphur.

In aqueous solutions of arsenous acid the sulphide forms more as a *yellow color* than as a precipitate, being soluble to quite an extent in pure water, especially when boiled (*5c*): $As_2S_3 + 3H_2O = As_2O_3 + 3H_2S$. This has been given as a method of separating arsenous sulphide from all other heavy metal sulphides (Clermont and Frommel, *J. C.*, 1879, **36**, 13). The precipitate is not formed in solutions of the arsenites except upon acidulation. The hydrogen sulphide converts the oxy salts of arsenic into the thio salt, which is decomposed by acid with precipitation of the sulphide of arsenic:

$$Na_3AsO_3 + 3H_2S = Na_3AsS_3 + 3H_2O$$
$$2Na_3AsS_3 + 6HCl = As_2S_3 + 3H_2S + 6NaCl$$

Alkali sulphides produce and, by further addition, dissolve the precipitate (*5c*):

$$2AsCl_3 + 3(NH_4)_2S = AS_2S_3 + NH_4Cl$$
$$As_2S_3 + 2(NH_4)S = (NH_4)_4As_2S_5 \text{ or } A_2S_3 + (NH_4)_2S = 2NH_4AsS_2$$

Arsenous sulphide is also soluble in alkali hydroxides and carbonates, with evolution of CO_2, forming arsenites and thioarsenites (*5c*). The thioarsenites are precipitated by acids forming As_2S_3 : $(NH_4)_4As_2S_5 + 4HCl = As_2S_3 + 2H_2S + 4NH_4Cl$ or $2NH_4AsS_2 + 2HCl = As_2S_3 + H_2S + 2NH_4Cl$.

The *solubility* of the sulphides of arsenic in *yellow ammonium sulphide* separates arsenic with antimony and tin from the other more common metals of the second group; and the solubility in ammonium carbonate effects an approximate separation from antimony and tin (Hager, *J. C.*, 1885, **48**, 838). Arsenous sulphide is soluble in solutions of alkali sulphites containing free sulphurous acid (separation from antimony and tin): $4As_2S_3 + 32KHSO_3 = 8KAsO_2 + 12K_2S_2O_3 + 3S_2 + 11SO_2 + 16H_2O$. It may also be separated from antimony and tin by boiling with strong hydrochloric acid, the As_2S_3 remaining practically insoluble; the sulphides of antimony and tin being dissolved. It is easily dissolved by strong

* Patrouillard (*Pharm. J. Trans.*, 1883, (3), **13**, 362) claims the reduction of As^v to As''' by oxalic acid; and Hager (*C. C.*, 1882, 690) reports a microscopic test for arsenic by reduction to metallic arsenic on boiling with oxalic and sulphuric acids. Experiments in the authors' laboratory fail to confirm these results.

hydrochloric acid, the As_2S_3 remaining practically insoluble: the sulphides of antimony and tin being dissolved. It is easily dissolved by strong nitric acid, and by free chlorine or nitrohydrochloric acid, as arsenic acid: $6As_2S_3 + 20HNO_3 + 8H_2O = 12H_3AsO_4 + 9S_2 + 20NO$; $2As_2S_3 + 10Cl_2 + 16H_2O = 4H_3AsO_4 + 3S_2 + 20HCl$. Usually a portion of the sulphur is oxidized to sulphuric acid, completely if the nitric acid or chlorine be in great excess and heat be applied: $As_2S_3 + 14Cl_2 + 20H_2O = 2H_3AsO_4 + 3H_2SO_4 + 28HCl$.

Arsenic pentasulphide, As_2S_5, is formed by passing H_2S for a long time into a solution of alkali arsenate and then adding acid (McCay, *Am.*, 1891, **12**, 547); by saturating a solution of *arsenic acid* with H_2S and placing, in stoppered bottle, in boiling water for one hour; or by passing a rapid stream of H_2S into an HCl solution of H_3AsO_4 (Bunsen, *A.*, 1878, **192**, 305; Brauner and Tomicek, *J. C.*, 1888, **53**, 146): $2H_3AsO_4 + 5H_2S + xHCl = As_2S_5 + 8H_2O + xHCl$. Carbon disulphide extracts no sulphur from the precipitate, indicating the absence of free sulphur. The presence of $FeCl_3$ or heating the solution does not reduce the As_2S_5 to As_2S_3. If there be a small amount of HCl and the H_2S be passed in slowly about 15 per cent of As_2S_3 is formed: $2H_3AsO_4 + 5H_2S + xHCl = As_2S_3 + S_2 + 8H_2O + xHCl$. If NH_4Cl be present more As_2S_3 is formed. According to Thiele (*C. C.*, 1890, 1, 877), arsenic acid cold treated with a slow stream of H_2S gives arsenous sulphide, while the hot acid with a rapid stream of the gas gives the pentasulphide. **Arsenic sulphide** has the same solubilities as arsenous sulphide. When distilled with hydrochloric acid gas and a reducing agent, arsenous chloride is formed ($AsCl_5$ is not known to exist). The solutions in the alkali hydroxides, carbonates and sulphides form arsenates and thioarsenates (5*c*). **Ammonium sulphide** added to a neutral or alkaline solution of arsenic acid forms arsenic sulphide which remains in solution as ammonium thioarsenate (5*c*). The addition of acid at once forms arsenic sulphide, not arsenous sulphide and sulphur. The reaction is much more rapid than with hydrosulphuric acid and is facilitated by warming.

Arsine, AsH_3, does not combine with hydrosulphuric acid until heated to 230°, while *stibine*, SbH_3, combines at the ordinary temperature (Brunn, *B.*, 1889, **22**, 3202).

Acidulated solutions of arsenic boiled with **thiosulphates** form *arsenous sulphide* (separation from Sb and Sn) (Lesser, *Z.*, 1888, **27**, 218). Arsenic may be removed from sulphuric acid by boiling with barium thiosulphate and no foreign material is introduced into the acid: $As_2O_3 + 3BaS_2O_3 = As_2S_3 + 3BaSO_4$; $2H_3AsO_4 + 5Na_2S_2O_3 = As_2S_3 + 5Na_2SO_4 + S_2 + 3H_2O$. (Thorn, *J. C.*, 1876, **29**, 517; Wagner, *Dingl.*, 1875, **218**, 321).

Sulphurous acid readily reduces arsenic acid to arsenous acid: $H_3AsO_4 + H_2SO_3 = H_3AsO_3 + H_2SO_4$ (Woehler, *A.*, 1839, **30**, 224).

f.—The arsenic from all arsenical compounds treated with concentrated **hydrochloric acid** and then distilled in a current of **hydrochloric acid gas**, passes into the distillate as *arsenous chloride*, $AsCl_3$. Nearly all of the arsenic will be carried over in the first 50 cc. of the distillate. This is a very accurate quantitative separation of arsenic from antimony and tin and from other non-volatile organic and inorganic material. The $AsCl_3$ passes over at 132°, condenses with **HCl** and may be tested with $SnCl_2$ (*g*), or, after decomposition with water (5*c*) by the usual tests for arsenous acid (Hufschmidt, *B.*, 1884, **17**, 2245; Beckurts, *Arch. Pharm.*, 1884, **222**, 684; Piloty and Stock, *B.*, 1897, **30**, 1649).

Hydrobromic acid in dilute solutions is without action upon the acids of arsenic. The concentrated acid reduces arsenic acid to arsenous acid: $H_3AsO_4 + 2HBr = H_3AsO_3 + Br_2 + H_2O$. **Hydriodic acid** reduces arsenic acid to arsenous acid with liberation of iodine. This is a method of detecting As^V in the presence of As'''. 0.0001 gram of H_3AsO_4 may be detected in the presence of one gram of As_2O_3: $2H_3AsO_4 + 4HI = As_2O_3 + 2I_2 + 5H_2O$ (Naylor, *J. C.*, 1880, **38**, 421).

Chloric and **bromic acids** oxidize arsenous compounds to arsenic acid with formation of the corresponding hydracid: $3As_2O_3 + 2HBrO_3 + 9H_2O = 6H_3AsO_4 + 2HBr$. **Iodic acid** oxidizes arsenous compounds to arsenic acid with liberation of iodine: $5As_2O_3 + 4HIO_3 + 13H_2O = 10H_3AsO_4 + 2I_2$.

g.—**Stannous chloride**, $SnCl_2$, reduces all compounds of arsenic from their hot concentrated hydrochloric acid solutions, as flocculent, black-brown, metalloidal *arsenic*, containing three or four per cent of tin. The arsenic, in solution with the concentrated hydrochloric acid, *acts* as arsenous chloride: $4AsCl_3 + 6SnCl_2 = As_4 + 6SnCl_4$. The hydrochloric acid should be 25 to 33 per cent; if not over 15 to 20 per cent, the reaction is slow and imperfect.

In a wide test-tube place 0.1 to 0.2 gram of the (oxidized) solid or solution to be tested, add about 1 gram of *sodium chloride*, and 2 or 3 cc. of *sulphuric acid*, then about 1 gram of crystallized *stannous chloride*; agitate, and heat to boiling several times, and set aside for a few minutes. Traces of arsenic give only a brown color; notable proportions give the flocculent precipitate. A dark gray precipitate may be due to mercury (§58, 6*g*), capable of being gathered into globules. If a precipitate or a darkening occurs, obtain conclusive evidence whether it contains arsenic or not, as follows: Dilute the mixture with ten to fifteen volumes of about 12 per cent hydrochloric acid; set aside, decant; gather the precipitate in a wet filter, wash it with a mixture of hydrochloric acid and *alcohol*, then with alcohol, then with a little ether, and dry in a warm place. A portion of this dry precipitate is now dropped into a small hard-glass tube, drawn out and closed at one end, and heated in the flame; arsenic is identified by its mirror (7), easily distinguished from mercury (§58, 7). Antimony is not reduced by stannous chloride; other reducible metals give no mirror in the reduction-tube. Small proportions of organic material impair the delicacy of this reaction, but do not prevent it. It is especially applicable to the hydrochloric acid distillate, obtained in separation of arsenic, according to *f*.

h.—**Chromates** boiled with *arsenites* and sodium bicarbonate give *chromium arsenate* (Tarugi, *J. C.*, 1896, **70**, ii, 340 and 390).

i.—**Magnesium salts** with ammonium chloride and ammonium hydroxide precipitate from solutions of arsenates, *magnesium ammonium arsenate*, $MgNH_4AsO_4$, white, easily soluble in acids. The reagents should be first mixed together, and used in a clear solution ("*magnesia mixture*") to make sure that enough ammonium salt is present to prevent the precipitation of magnesium hydroxide by the ammonium hydroxide. The crystalline precipi-

tate forms slowly but completely. Compare with the corresponding magnesium ammonium phosphate (§189, 6*d*). *Magnesium arsenite* is insoluble in water, but is soluble in ammonium hydroxide and in ammonium chloride (distinction from arsenates).

j.—**Silver nitrate** solution precipitates from neutral solutions of arsenites, or ammonio-silver nitrate * precipitates from a water solution of arsenous oxide, *silver arsenite*, Ag_3AsO_3, yellow, readily soluble in dilute acids or in ammonium hydroxide (§59, 6*g*). Neutral solutions of *arsenates* are precipitated as *silver arsenate*, Ag_3AsO_4, reddish brown, having the same solubilities as the arsenite.

k.—**Copper sulphate** solution precipitates from neutral solutions of arsenites, or ammonio-copper sulphate (prepared in the same manner as the ammonio-silver oxide described above) precipitates from water solutions of arsenous oxide, the *green copper arsenite*, $CuHAsO_3$ (Scheele's green), soluble in ammonium hydroxide and in dilute acids. **Copper acetate**, in boiling solution, precipitates the *green copper aceto-arsenite* $(CuOAs_2O_3)_3Cu(C_2H_3O_2)_2$ (Schweinfurt green), soluble in ammonium hydroxide and in acids. Both these salts are often designated as Paris green (§77, 6*g*). Copper sulphate with excess of free alkali is reduced to cuprous oxide with formation of alkali arsenate (10). $K_3AsO_3 + 2CuSO_4 + 4KOH = K_3AsO_4 + 2K_2SO_4 + Cu_2O + 2H_2O$. Solutions of arsenates are precipitated by copper sulphate as copper arsenate, $CuHAsO_4$, greenish blue, the solubilities and conditions of precipitation being the same as for the arsenites.

l.—**Ferric salts** precipitate from arsenites, and freshly precipitated ferric hydroxide (used as an antidote, Wormley, 246), forms with arsenous oxide, variable basic ferric arsenites, scarcely soluble in acetic acid, soluble in hydrochloric acid. Water slowly and sparingly dissolves from the precipitate the arsenous anhydride; but a large excess of the ferric hydroxide holds nearly all the arsenic insoluble. To some extent the basic ferric arsenites are transposed into basic ferrous arsenates, insoluble in water, in accordance with the reducing power of arsenous oxide. In the presence of alkali acetates, arsenic acid, or acidulated solutions of arsenates, are precipitated by ferric salts as ferric arsenate, $FeAsO_4$, yellowish white, insoluble in acetic acid (compare §126, 6*d*).

m.—Ammonium molybdate, $(NH_4)_2MoO_4$, in nitric acid solution, when slightly warmed with a solution of arsenic acid or of arsenates gives a yellow precipitate of *ammonium arseno-molybdate*, of variable composition. No precipitate is formed with As'''. This precipate is very similar in appearance and properties to the ammonium phospho-molybdate; except the latter precipitates completely in the cold.

6′. **Special Reactions.** *a*.—**Marsh's Test.**—This is an extremely delicate test for arsenic, especially adapted for the detection of this element when present in small quantities, even when large quantities of other elements are present. Arsenic, from all of its soluble compounds, is reduced by the action of dilute sulphuric or hydrochloric **acid on zinc,** forming at first metallic arsenic and then *arsenous hydride*, AsH_3, gaseous: $As_2O_3 + 6Zn + 6H_2SO_4 = 2AsH_3 + 6ZnSO_4 + 3H_2O$; $H_3AsO_4 + 4Zn + 4H_2SO_4 = AsH_3 + 4ZnSO_4 + 4H_2O$. The arsenic is precipitated with the other metals of the second group by **hydrogen sulphide,** separated with antimony, tin (gold, platinum and molybdenum) by **yellow ammonium sulphide.** This solution is precipitated by dilute **hydrochloric acid** and the mixed sulphides, well *washed*,† are dissolved in **hydrochloric acid** using as small an amount of **potassium chlorate** crystals as possible. The solution is boiled (till it does not bleach litmus paper)

* Prepared by adding ammonium hydroxide to a solution of silver nitrate till the precipitate at first produced is nearly all redissolved.

† If the ammonium salts are not thoroughly removed by washing there is danger of the formation of the very explosive chloride of nitrogen (§ **268,** 1) when the precipitate is treated with hydrochloric acid and potassium chlorate.

to remove excess of chlorine and is then ready for the **Marsh apparatus.** This apparatus consists of a strong Erlenmeyer flask of about 125 cc. capacity fitted with a two hole rubber stopper. Through one hole is passed a thistle (safety) tube, reaching nearly to the bottom of the flask; in the other is fitted a three-inch Marchand calcium chloride tube, which projects just through the stopper and is filled with glass-wool and granular calcium chloride to dry the gases generated in the flask. To the other end of the Marchand tube is fitted, with a small cork or rubber stopper, a piece of hard glass tubing of six mm. diameter and one foot long. This tube should be constricted one-half, for about two inches, beginning at the middle of the tube and extending toward the end not fastened to the calcium chloride tube. The outer end of the tube should also be constricted to about one mm. inner diameter. A short piece of rubber tubing should connect this constricted end with a piece of ordinary glass tubing, dipping into a test tube about two-thirds filled with a two per cent solution of silver nitrate. The rubber tubing should make a close joint with the constricted end of the hard glass tube, and yet not fit so snug but that it can be easily removed.

From 10 to 20 grams of **granulated zinc** * are placed in the flask with sufficient water to cover the end of the thistle tube. Four or five cubic centimeters of reagent sodium carbonate are added and the stopper tightly fitted to the flask. Dilute sulphuric acid (one of acid to three of water) should now be added, very carefully at first,† until a moderate evolution of hydrogen is obtained.

The hydrogen should be allowed to bubble through the silver nitrate for about five minutes. There should be no appreciable blackening of the solution (§**59**, 10), thus proving the absence of arsenic from the zinc and the sulphuric acid. The purity of the reagents having been established the solution containing the arsenic may be added in small amounts at a time through the thistle tube. If arsenic be present there will be almost immediate blackening of the silver nitrate solution.

$$6AgNO_3 + AsH_3 + 3H_2O = 6Ag + H_3AsO_3 + 6HNO_3$$

The hard glass tube should now be heated ‡ to redness by a flame from

* The zinc and all the reagents should be absolutely free from arsenic. If the zinc be strictly chemically pure it will be but slowly attacked by the acid. It should be platinized (§**219**, 4a) or should contain traces of iron. Hote (*A. Ch.*, 1884, (6), 3, 141) removes arsenic from zinc by adding anhydrous $MgCl_2$ to the molten metal, $AsCl_3$ being evolved. The zinc purified in this way is readily attacked by acids.

† The acid first added decomposes the alkali carbonate forming carbon dioxide which rapidly displaces the air and greatly lessens the danger of explosion when the gas is ignited. If too much acid be added before the carbonate is decomposed violent frothing may take place and the liquid contents of the flask forced into the calcium chloride tube.

‡ Before heating the tube or igniting the gas, a towel should be wrapped around the flask to insure safety in case of an explosion due to the imperfect removal of the air; or the tube connecting the hard glass tube with the Marchand tube should be of larger size and provided with a plug of wire gauze (made of 10 or 20 circles of gauze the size of the tube). A flame cannot pass such a plug of wire gauze.

a Bunsen burner provided with a flame spreader. The flame should be applied to the tube between the calcium chloride tube and the constricted portion. The tube should be supported to prevent sagging in case the glass softens, and it is customary to wrap a few turns of wire gauze around the portion of the tube receiving the heat. The heat of the flame decomposes the arsine and a **mirror** of *metallic arsenic* is deposited in the constricted portion of the tube just beyond the heated portion. This may be tested as described under *c* 1. When a sufficient mirror has been obtained the flame is withdrawn, and, removing the rubber tube, the escaping gas * is ignited. As small a quantity of arsenic as 0.002 mg. will produce a visible mirror and if 20 g. of material is used for analysis, this would represent one part of arsenic in 10,000,000 parts.

b. **Arsenous Hydride** (arsine), AsH_3, burns when a stream of it is ignited where it enters the air, and explodes when its mixture with air is ignited. It burns with a somewhat luminous and slightly bluish flame (distinction from hydrogen); the hydrogen being first oxidized, and the liberated arsenic becoming incandescent, and then undergoing oxidation: the vapors of water and arsenous anhydride passing into the air: $2AsH_3 + 3O_2 = As_2O_3 + 3H_2O$. If present in considerable quantity a white powder may be observed settling on a piece of black paper placed beneath the flame. If the cold surface of a porcelain dish be brought in contact with the flame the oxidation is prevented and lustrous black or brownish-black **spots** of *metallic arsenic* are deposited on the porcelain surface: $4AsH_3 + 3O_2 = As_4 + 6H_2O$. A number of spots should be obtained and all the tests for metallic arsenic applied. The arsenic in the silver nitrate solution is present as arsenous acid and can be detected by the usual tests (6*c*) by first removing the excess of silver nitrate with dilute hydrochloric acid or calcium chloride, or by cautiously neutralizing with ammonia the arsenic may be precipitated as the yellow silvery arsenite (6*j*).

To generate arsine, magnesium or iron † may be used, instead of zinc, and hydrochloric acid instead of sulphuric acid. Arsine cannot be formed in the presence of oxidizing agents as the halogens, nitric acid, chlorates, hypochlorites, etc. Arsinuretted hydrogen (arsine) may also be produced from *arsenous compounds* by nascent hydrogen generated in alkaline solution. Sodium amalgam,‡ zinc (or zinc and magnesium) and potassium hydroxide or aluminum and potassium hydroxide may be used as the reducing agent. There is

* Arsine is an exceedingly poisonous gas, the inhalation of the unmixed gas being quickly fatal. Its dissemination in the air of the laboratory, even in the small portions which are not appreciably poisonous, should be avoided. Furthermore, as it is recognized or determined, in its various analytical reactions, only by its decomposition, to permit it to escape undecomposed is so far to fail in the object of its production. The evolved gas should be constantly run into silver nitrate solution, or kept burning.

† According to Thiele (C. C., 1890, 1, 877) arsenic may be separated from antimony in the Marsh test by using electrolytically deposited iron instead of zinc. Stibine is not evolved. According to Sautermeister (*Analyst*, 1891, 218) arsine is not produced when hydrochloric acid acts upon iron containing arsenic, but if several grams of zinc be added a very small amount of arsenic in the iron may be detected.

‡ Sodium amalgam is conveniently prepared by adding (in small pieces at a time) one part of sodium to eight parts (by weight) of dry mercury warmed on the water bath. When cold the amalgam becomes solid and is easily broken. It should be preserved in well stoppered bottles.

no reaction with As^V, or with compounds of antimony (§70, 6*j*); hence when the arsenic is present in the triad condition (As^V may be reduced to As''' by SO_2) the use of one of the above reagents serves admirably for the detection of arsenic in the presence of antimony. This experiment may be made in a test-tube, the arsenic being detected by covering the tube with a piece of filter paper moistened with silver nitrate. It is very difficult to drive over the last traces of the arsenic and therefore the method is not satisfactory for quantitative work (Hager, *J. C.*, 1885, **48**, 838; Johnson, *C. N.*, 1878, **38**, 301; and Clark, *J. C.*, 1893, **63**, 884).

If ferrous sulphide contains metallic iron and arsenic, arsine may be generated with the hydrogen sulphide. It cannot be removed by washing the gases with hydrochloric acid (Otto, *B.*, 1883, **16**, 2947).

Arsine does not combine with hydrogen sulphide until heated to 230°, while *stibine*, SbH_3, combines at ordinary temperature (method of separation) (Brunn, *B.*, 1889, **22**, 3202; Myers, *J. C.*, 1871, **24**, 889). As dry hydrogen sulphide is without action upon dry iodine, it may be freed from arsine by passing the mixture of the dried gases through a tube filled with glass wool interspersed with dry iodine. $AsH_3 + 3I_2 = AsI_3 + 3HI$ (Jacobson, *B.*, 1887, **20**, 1999). Arsenous hydride is decomposed by passing through a tube heated to redness (mirror in Marsh test) $4AsH_3 = As_4 + 6H_2$. Nitric acid oxidizes it to arsenic acid, $3AsH_3 + 8HNO_3 = 3H_3AsO_4 + 8NO + 4H_2O$; and may be used instead of silver nitrate to effect a separation of arsine and stibine in the Marsh test. The nitric acid solution is evaporated to dryness and the residue thoroughly washed with water. Test the solution for arsenic with silver nitrate and ammonium hydroxide (Ag_3AsO_4, reddish brown precipitate, 6*f*). Dissolve the residue in hydrochloric or nitrohydrochloric acid and test for antimony with hydrogen sulphide (Ansell, *J. C.*, 1853, **5**, 210).

c.—**Comparison of the mirrors and spots obtained with arsenic and antimony.**—1. Both the **mirror** and **spots** obtained in the Marsh test exhibit the properties of elemental arsenic (5*a*). The reactions of these deposits having analytical interest are such as distinguish arsenic from antimony.

Arsenic Mirror.	Antimony Mirror.
Deposited beyond the flame; arsene not being decomposed much below a red heat.	Deposited before or on both sides of the flame; stibine being decomposed considerably below a red heat.
Volatilizes in absence of air at 450° (1), allowing the mirror to be driven along the tube; it does not melt.	The mirror melts to minute globules at 630°, and is then driven at a red heat.
By vaporization in the stream of gas, escapes with a garlic odor.	The vapor has no odor.
By slow vaporization in a current of air a deposit of octahedral and tetrahedral crystals is obtained, forming a white coating soluble in water and giving the reactions for arsenous oxide.	By vaporization in a current of air, a white amorphous coating is obtained; insoluble in water, soluble in hydrochloric acid, and giving reactions for antimonous oxide.

The heated mirror combines with hydrogen sulphide, forming the lemon-yellow arsenous sulphide, which, being volatile, is driven to the cooler portion of the tube.

The dry sulphide is not readily attacked by dry hydrochloric acid gas (6*f*).

Arsenic Spots.

Of a steel gray to black lustre.

Volatile by oxidation to arsenous oxide at 218°.

Dissolve in hypochlorite.*

Warmed with a drop of ammonium sulphide form yellow spots, soluble in ammonium carbonate, insoluble in hydrochloric acid (6*e*).

With a drop of hot nitric acid, dissolve clear. The clear solution, with a drop of solution of silver nitrate, when treated with vapor of ammonia, gives a brick-red precipitate.

The solution gives a yellow precipitate when warmed with a drop of ammonium molybdate.

With vapor of iodine, color yellow, by formation of arsenous iodide, readily volatile when heated.

The heated mirror combines with hydrogen sulphide forming the orange antimonous sulphide, which is not readily volatile.

The sulphide is readily decomposed by dry hydrochloric acid gas, forming antimonous chloride which is volatile, and may be driven over the unattacked arsenous sulphide.

Antimony Spots.

Of a velvety brown to black surface.

Volatile, by oxidation to antimonous oxide, at a red heat.

Do not dissolve in hypochlorite.

Warmed with ammonium sulphide, form orange-yellow spots, insoluble in ammonium carbonate, soluble in hydrochloric acid (§70. 6*e*).

With a drop of hot dilute nitric acid, turn white. The white fleck, by action of nitric acid treated with silver nitrate and vapor of ammonia, gives no color until warmed with a drop of ammonium hydroxide, then gives a black precipitate.

With the white fleck no further action on addition of ammonium molybdate.

With vapor of iodine, color more or less carmine-red, by formation of antimonous iodide, not readily volatile by heat.

* The hypochlorite reagent, usually **NaClO**, decomposes in the air and light on standing. It should instantly and perfectly bleach litmus paper (not redden it). It dissolves arsenic by oxidation to arsenic acid. $As_4 + 10NaClO + 6H_2O = 4H_3AsO_4 + 10NaCl$.

2. To the spot obtained on the porcelain surface, add a few drops of nitric acid and heat; then add a drop of ammonium molybdate. A yellow precipitate indicates arsenic. Antimony may give a white precipitate with the nitric acid, but gives no further change with the ammonium molybdate (Deniges, *C. r.*, 1890, **111,** 824).

3. Oxidize the arsenic spot with nitric acid and evaporate to dryness. Add a drop of silver nitrate or ammonio-silver nitrate (6*j*). A reddish-brown precipitate indicates arsenic.

4. After the formation of the **mirror** in Marsh's test the generating flask may be disconnected and a stream of dry hydrogen sulphide passed over the heated mirror. If the mirror consists of both arsenic and antimony, the sulphides of both these metals will be formed, and as the arsenous sulphide is volatile when heated, it will be deposited in the cooler portion of the tube. The sulphides being thus separated can readily be distinguished by the color. If now a current of dry hydrochloric acid gas be substituted for the hydrogen sulphide the antimonous sulphide will be decomposed to the white antimonous chloride which volatilizes and may be driven past the unchanged arsenous sulphide (5*c*).

5. The tube containing the mirror is cut so as to leave about two inches on each side of the mirror and left open at both ends. Incline the tube and beginning at the lower edge of the mirror gently heat, driving the mirror along the tube. The mirror will disappear and if much arsenic be present a white powder will be seen forming a ring just above the heated portion of the tube. This powder consists of crystals of arsenous oxide, and should be carefully examined under the microscope and identified by their crystalline form (Wormley, 270).

6. The crystals of arsenous oxide obtained above are dissolved in water and treated with ammonio-silver nitrate forming the yellow silver arsenite (6*j*): or with ammonio-copper sulphate forming the green copper arsenite (6*k*) (Wormley, 259). Any other test for arsenous oxide may be applied as desired.

7. Magnesia mixture (6*i*) is added to the solution of the mirror or spots in nitric acid. The solution must be strongly alkaline. A white crystalline precipitate of magnesium ammonium arsenate, $MgNH_4AsO_4$, is formed (Wormley, 316).

d.—**Reinsch's Test.**—If a solution of arsenic be boiled with hydrochloric acid and a strip of bright copper foil, the arsenic is deposited on the copper as a gray film. Hager (*C. C.*, 1886, 680) recommends the use of brass foil instead of copper foil. When a large amount of arsenic is present the coating of arsenic separates from the copper in scales. The film does not consist of pure metallic arsenic, but appears to be an alloy of arsenic and copper. Arsenous compounds are reduced much more readily than arsenic compounds. The hydrochloric acid should compose at least one-tenth the volume of the solution. The arsenic is not deposited if the acid is not present. This serves as one of the most satisfactory methods of determining the presence or absence of arsenic in

hydrochloric acid. Dilute the concentrated acid with five parts of water and boil with a thin strip of bright copper foil. A trace of arsenic if present will soon appear on the foil. For further identification of the deposit, wash the foil with distilled water, dry, and heat in a hard glass tube, as for the oxidation of the arsenic mirror (6′*c*, 5). The crystals may be identified by the microscope and by any other tests for arsenous oxide. It is important that the surface of the copper should be bright. This is obtained by rubbing the surface of the foil with a file, a piece of pumice or sand-paper just before using. The copper should not contain arsenic, but if it does contain a small amount no film will be deposited due to its presence unless agents are present which cause partial solution of the foil. If a strip of the foil, upon boiling with hydrochloric acid for ten minutes, shows no dimming of the brightness of the copper surface; the purity of both acid and copper may be relied upon for the most exact work. Antimony, mercury, silver, bismuth, platinum, palladium and gold are deposited upon copper when boiled with hydrochloric acid. Under certain conditions most of these deposits may closely resemble that of arsenic. Of these metals mercury is the only one that forms a sublimate when heated in the reduction tube (7), and this is readily distinguished from arsenic by examination under the microscope. Antimony may be volatilized as an amorphous powder at a very high heat. Organic material may sometimes give a deposit on the copper which also yields a sublimate, but this is amorphous and does not show the octahedral crystals when examined under the microscope (Wormley, 269 and ff.; Clark, *J. C.*, 1893, **63**, 886).

c.—**Detection in Case of Poisoning.**—Arsenic in its various compounds is largely used as a poison for bugs, rodents, etc., and frequently cases arise of accidental arsenical poisoning. It is also used for intentional poisoning, chiefly suicidal. It is usually taken in the form of arsenous oxide (white arsenic), or "Fowler's Solution" (a solution of the oxide in alkali carbonate). One hundred fifty to two hundred milligrams (two to three grains) are usually sufficient to produce death. Violent vomiting is a usual symptom and death occurs in from three to six hours. In cases of suspected poisoning vomiting should be induced as soon as possible by using an emetic followed by demulcent drinks, or the stomach should be emptied by a stomach pump. Freshly prepared ferric hydroxide is the usual antidote, of which twenty-five to fifty grams (one to two ounces) may be given. The antidote may be prepared by adding magnesia (magnesium oxide), ammonium hydroxide, or cooking soda (sodium bicarbonate) to ferric chloride or muriate tincture of iron; straining in a clean piece of muslin, and washing several times. If magnesia be used it is not necessary to wash, as the magnesium chloride formed is helpful rather than injurious. A portion of the ferric hydroxide oxidizes some of the arsenous compound, being itself reduced to the ferrous condition, and forming an insoluble ferrous arsenate. When the ferric oxide is in excess the ferrous arsenate does not appear to be acted upon by the acids of the stomach. Of course it will be seen that the ferric hydroxide will have no effect upon the arsenic which has entered into the circulation.

It frequently becomes necessary for the chemist to analyze portions of suspected food, contents of the stomach, urine; or, if death has ensued, portions of the stomach, intestines, liver, or other parts of the body. At first a careful examination should be made of the material at hand for solid white particles, that would indicate arsenous oxide. If particles be found they can at once be identified by the usual tests. Liquid food or liquid contents of the stomach should be boiled with dilute hydrochloric acid, filtered and washed and the filtrate precipitated with hydrogen sulphide, etc. When solid food or portions of tissue are to be analyzed, it is necessary first to destroy the organic material. Several methods have been proposed:

(1) **Method of Fresenius and Babo.**—The tissue is cut into small pieces and about an equal weight of pure hydrochloric acid added to this, enough water should be added to form a thin paste and dilute the hydrochloric acid five or six times. The mass is heated on the water bath and crystals of potassium chlorate added in small amounts at a time with stirring until a clear yellow liquid is obtained containing a very small amount of solid particles. The heating is continued until there is no odor of chlorine, but concentration should be avoided by the addition of water. The solution should be cooled and filtered,

the arsenic now being present in the filtrate as arsenic acid. This solution should be treated with sodium bisulphite or sulphur dioxide to reduce the arsenic acid to arsenous acid and then the arsenic may be precipitated with hydrogen sulphide. It is advisable to pass the hydrogen sulphide through the warm liquid for twenty-four hours to insure complete precipitation. A yellowish precipitate of organic matter will usually be obtained even if arsenic be absent. The precipitate should be filtered, washed, and then dissolved in dilute ammonium hydroxide, which separates it from other sulphides of the silver, tin and copper groups, that may be present. A portion at least of the precipitated organic matter will dissolve in the ammonium hydroxide. The filtrate should be acidulated with hydrochloric acid, filtered and washed. Dissolve the precipitate in concentrated nitric acid and evaporate to dryness. Redissolve in a small amount of water, add a drop of nitric acid, filter and test the filtrate by Marsh's test or any of the other tests for arsenic.

(2) **Hydrochloric acid** diluted alone may be used for the disintegration of the soft animal tissues. The solution will usually be dark colored and viscous and not at all suited for further treatment with hydrogen sulphide; but may be at once subjected to the Reinsch test (6*d*).

(3) **Method of Danger and Flandin.**—The tissue may be destroyed by heating in a porcelain dish with about one-fourth its weight of concentrated sulphuric acid. When the mass becomes dry and carbonaceous it is cooled, treated with concentrated nitric acid and evaporated to dryness. Moisten with water, add nitric acid, and again evaporate to dryness; and repeat until the mass is colorless. Dissolve in a small amount of water and test for arsenic by the usual tests. This method is objectionable if chlorides are present as the volatile arsenous chloride will be formed.

(4) Method by **distillation** with hydrochloric acid. The finely divided tissue is treated, in a retort, with its own weight of concentrated hydrochloric acid and distilled on the sand bath. Salt and sulphuric acid may be used instead of hydrochloric acid. A receiver containing a small amount of water is connected to the retort and the mass distilled nearly to dryness. If preferred, gaseous hydrochloric acid may be conducted into the retort during the process of distillation, in which case all the arsenic (even from arsenous sulphide (5*c*)) will be carried over in the first 100 cc. of the distillate. The receiver contains the arsenic, a great excess of hydrochloric acid and a small amount of organic matter. To a portion of this solution the Reinsch test may be applied at once and other portions may be diluted and tested with hydrogen sulphide or the solution may at once be tested in the Marsh apparatus.

For more detailed instructions concerning the detection and estimation of arsenic in organic matter, special works on Toxicology and Legal Medicine must be consulted. The following are valuable works on this subject: Medical Jurisprudence. - Forensic Medicine and Toxicology, Witthaus and Becker, Vol. iv, 1911; Laboratory Manual for the Detection of Poisons and Powerful Drugs, Dr. Wilhelm Autenreith (translated by Wm. H. Warren), 1915; Allen's Commercial Organic Analysis, Vol. vi (4th edition, 1912); The Qualitative Analysis of Medicinal Preparations, H. C. Fuller, 1912; Elementary Chemical Microscopy, Emile M. Chamot, 1915; Biochemisches Handlexikon, V. Band, Dr. Emil Abderhalden, 1911; Mikrochemische Analyse, I and II Teil, P. D. C. Kley, 1915; Medical Jurisprudence, Taylor; Ermittelung von Giften, Dragendorff.

7. **Ignition.**—Metallic arsenic is obtained by igniting any compound containing arsenic with potassium carbonate and charcoal,* or with potassium cyanide:

$$2As_2O_3 + 6KCN = As_4 + 6KCNO$$
$$2As_2S_3 + 6KCN = As_4 + 6KCNS$$
$$2As_2S_3 + 6Na_2CO_3 + 6KCN = As_4 + 6Na_2S + 6KCNO + 6CO_2.$$
$$4H_3AsO_4 + 5C = As_4 + 5CO_2 + 6H_2O$$

* A very suitable carbon for the reduction of arsenic is obtained by igniting an alkali tartrate in absence of air to complete carbonization.

If this ignition be performed in a small reduction-tube * (a hard glass tube about 7 mm. in diameter, drawn out and sealed at one end), the reduced arsenic sublimes and condenses as a mirror in the cool part of the tube. The test may be performed in the presence of mercury compounds, but more conveniently after their removal; in presence of organic material, it is altogether unreliable. If much free sulphur be present the arsenic should be removed by oxidation to arsenic acid by nitric acid or hydrochloric acid and potassium chlorate, then precipitation after addition of ammonium hydroxide by magnesium mixture and thoroughly drying before mixing with the cyanide or other reducing agent.

8. **Detection.**—Arsenic is precipitated, from the solution acidulated with hydrochloric acid, in the second group by hydrosulphuric acid as the sulphide (6*e*). By its solution in (yellow) ammonium sulphide it is separated from **Hg**, **Pb**, **Bi**, **Cu**, and **Cd**. By reduction to arsine in the Marsh apparatus it is separated with antimony from the remaining second group metals. The decomposition of the arsine and stibine with silver nitrate precipitates the antimony, thus effecting a separation from the arsenic, which passes into solution as arsenous acid. The excess of $AgNO_3$ is removed by **HCl** or $CaCl_2$ and the presence of arsenic confirmed by its precipitation with H_2S. For other methods of detection consult the text (6, 6′ and 7). For distinction between As^V and As''' see (6 and §88, 4).

9. **Estimation.**—(*1*). As lead arsenate, $Pb_3(AsO_4)_2$. To a weighed portion of the solution containing arsenic acid, a weighed amount of **PbO** is added. After evaporation and ignition at a dull red heat the residue is weighed as $Pb_3(AsO_4)_2$ from which the weight of the added **PbO** is subtracted. The difference shows the amount of arsenic present reckoned as As_2O_5. (*2*). It is precipitated by $MgSO_4$ in presence of NH_4OH and NH_4Cl, and after drying at 103°, weighed as $MgNH_4AsO_4.H_2O$; antimony is not precipitated if a tartrate be present (Lesser, *Z.*, 1888, **27**, 218). (*3*). The $MgNH_4AsO_4$ is converted by ignition into $Mg_2As_2O_7$, and weighed. (*4*). The solution of arsenous acid containing **HCl** is precipitated by H_2S.

* As much of the reduction-glass tubing contains arsenic (?) Fresenius (*Z.*, **20**, 531 and **22**, 397) recommends the following modification of the above method: A piece of reduction tubing about 16 mm. diameter and 15 cm. long is drawn out to a narrow tube at one end. The other end of the tube is connected with a suitable apparatus for generating and drying carbon dioxide. The sample to be tested is thoroughly dried and mixed with the dry cyanide (or charcoal) and carbonate, placed in a small porcelain combustion boat and put in the middle of the reduction tube. The air is then driven from the tube by the dry carbon dioxide and the whole heated gently until all moisture is expelled. The tube is then heated to redness near the point of constriction and when this is done the boat is heated, gently at first to avoid spattering of the fusing mass, then to a full redness till all the arsenic has been driven out. During the whole of the experiment a gentle stream of carbon dioxide is passed through the tube. The arsenic collects as a mirror in the narrow part of the tube just beyond the heated portion. The small end of the tube may now be sealed, the mirror collected by a gentle flame, driven to any desired portion of the tube and tested with the usual tests (6′ c5). Compounds of antimony when treated in this way do not give a mirror. As small an amount as 0.00001 gram of As_2O_3 will give a distinct mirror by this method.

The precipitate is separated from free sulphur by solution in NH_4OH and reprecipitated with **HCl**. It is then dried at 100° and weighed as As_2S_3. (*5*). By precipitation as in (*4*) and removal of sulphur by washing with CS_2. Dry at 100° and weigh as As_2S_3. (*6*). Uranyl acetate, in presence of ammonium salts, precipitates $NH_4UO_2AsO_4$; by ignition this is converted into uranyl pyroarsenate $(UO_2)_2As_2O_7$, and weighed as such. (*7*). Small amounts may be converted into the metallic arsenic mirror by the Marsh apparatus and weighed or compared with standard mirrors (Gooch and Moseley, *C. N.*, 1894, **70**, 207). (*8*). As‴ is converted into As^V by a graduated solution of iodine in presence of $NaHCO_3$. The end of the reaction is shown by the blue color imparted to starch. (*9*). As‴ is oxidized to As^V by a graduated solution of $K_2Cr_2O_7$, and the excess of $K_2Cr_2O_7$ determined by a graduated solution of $FeSO_4$. (*10*). As‴ is converted to As^V by a weighed quantity of $K_2Cr_2O_7$ with **HCl**, and the excess of chlorine is determined by **KI** and $Na_2S_2O_3$. (*11*). As‴ is oxidized to As^V by a graduated solution of $KMnO_4$. The end of the reaction is indicated by the color of the $KMnO_4$. (*12*). As^V is reduced to As‴ by a graduated solution of **HI**. The action takes place in acid solutions. (*13*). In neutral solution, as arsenate, add an excess of standard $AgNO_3$, and in an aliquot part estimate the excess of $AgNO_3$ with standard **NaCl**. (*14*). Distillation as $AsCl_3$ (Piloty and Stock, *B.*, 1897, **30**, 1649; see also 6′*e* 4). (*15*). The arsenic compound is converted into AsH_3 and this passed into a solution of standard silver nitrate, the excess of which is estimated with standard **NaCl** or the excess of $AgNO_3$ is removed and the arsenous acid titrated as in methods (*9*) or (*11*). (*16*). Small amounts are determined by conversion to AsH_3 and the stain produced on mercury bromide paper compared with the stain produced by known amounts of arsenic. (Seeker and Smith, *U. S. Bull.* No. 147, p. 212-214). Many other methods have been recommended.

10. **Oxidation.**—$As^{-'''}H_3$ is oxidized to As‴ by $AgNO_3$, H_2SO_3, H_2SO_4, and HIO_3; and to As^V by $KMnO_4$ (Tivoli, *Gazzetta*, 1889, **19**, 630), HNO_2, HNO_3, **Cl** and **Br** (Parsons, *C. N.*, 1877, **35**, 235). As° is oxidized to As‴ by H_2O_2 (Clark, *J. C.*, 1893, **63**, 886), HNO_3, H_2SO_4 hot, **Cl**, **HClO**, $HClO_3$, **Br**, $HBrO_3$, HIO_3, Ag′ (Senderens, *C. r.*, 1887, **104**, 175), and to As^V by the same reagents in excess except H_2SO_4 and Ag′, which oxidize to As‴ only. As‴ is also oxidized to As^V in presence of acid by PbO_2, Cr^{VI}; by compounds of **Co**, **Ni**, and **Mn**, with more than two bonds; and in alkaline mixture by PbO_2, Hg_2O, **HgO**, **CuO**, K_2CrO_4, $K_3Fe(CN)_6$, etc. (Mayer, *J. pr.*, 1880 (2), **22**, 103). Arsine is oxidized to metallic arsenic by $HgCl_2$ (Magençon and Bergeret, *J. C.*, 1874, **27**, 1008), and by As‴, the As‴ also becoming As° (Tivoli, *C. C.*, 1887, 1097). As^V and As‴ are reduced to metallic arsenic by fusion with **CO**, with free carbon, or with carbon combined, as $H_2C_2O_4$, **KCN**, etc. (7). By $SnCl_2$ (6*g*) and H_3PO_2 (6*d*) in strong **HCl** solution; also with greater or less completeness by some free metals, such as **Cu**, **Cd**, **Zn**, **Mg**, etc. Rideal (*C. N.*, 1885, **51**, 292) recommends

HCl solution; also with greater or less completeness by some free metals, such as **Cu**, **Cd**, **Zn**, **Mg**, etc. Rideal, (*C. N.*, 1885, **51**, 292) recommends the use of the copper-iron wire couple for the detection of small quantities of arsenic by reduction to the elemental state. 0.000005 grams may be detected. In solution As^{V} is reduced to As''' by H_3PO_2, H_2S, H_2SO_3, $Na_2S_2O_3$ (6*e*), HCl, HBr, HI (6*f*), HCNS, etc. As^{V} and As''' are reduced to $As^{-'''}H_3$ by nascent hydrogen generated by the action of Zn and dilute H_2SO_4, or, in general, by any metal and acid which will give a ready generation of hydrogen, as Zn, Sn, Fe, Mg, etc., and H_2SO_4 and HCl (Draper, *Dingl.*, 1872, **204**, 320). As''' is reduced to $As^{-'''}H_3$ by nascent hydrogen generated in alkaline solution as, Al and KOH, Zn and KOH, sodium amalgam, etc. (separation from antimony) (Davy, *Ph. C.*, 1876, **17**, 275; Johnson, *C. N.*, 1878, **38**, 301).

§70. Antimony (Stibium) Sb = 120.2. Valence three and five (§11).

1. **Properties.**—*Specific Gravity*, 6.62 (*Z. anorgan. Chem.*, 1902, 177). *Melting point*, 630° (*Cir. B. S.*, **35**, 1915). *Boiling point*, between 1500° and 1700° (*B.*, 1889, 725). Its molecular weight is unknown, as its vapor density has not been taken. Antimony is a lustrous, silver white, brittle and readily pulverizable metal. It is but little tarnished in dry air and oxidizes slowly in moist air, forming a blackish gray mixture of antimony and antimonous oxide. At a red heat it burns in the air or in oxygen with incandescence, forming white inodorous (distinction from arsenic) vapors of antimonous oxide.

2. **Occurrence.**—Native in considerable quantities in northern Queensland, Australia (Mac Ivor, *C. N.*, 1888, **57**, 64); as stibnite, Sb_2S_3; as valentinite, Sb_2O_3; in very many minerals usually combined with other metals as a double sulphide (Campbell, *Phil. Mag.*, 1860, (4), **20**, 304; **21**, 318).

3. **Preparation.** (*a*) The sulphide is converted into the oxide by roasting in the air, and then reduced by fusion with coal or charcoal. (*b*) The sulphide is fused with charcoal and sodium carbonate: $2Sb_2S_3 + 6Na_2CO_3 + 3C = 4Sb + 6Na_2S + 9CO_2$. (*c*) It is reduced by metallic iron: $Sb_2S_3 + 3Fe = 2Sb + 3FeS$. (*d*) To separate it from other metals with which it is frequently combined requires a special process according to the nature of the ore (Dexter, *J. pr.*, 1839, **18**, 449; Pfeifer, *A.*, 1881, **209**, 161).

4. **Oxides.** Antimony forms three oxides, Sb_2O_3, Sb_2O_4, and Sb_2O_5. (*a*) Antimonous oxide, Sb_2O_3, is formed (*1*) by the action of dilute nitric acid upon Sb°; (*2*) by precipitating $SbCl_3$ with Na_2CO_3 or NH_4OH; (*3*) by dissolving Sb° in concentrated H_2SO_4 and precipitating with Na_2CO_3; (*4*) by burning antimony at a red heat in air or oxygen; (*5*) by heating Sb_2O_4 or Sb_2O_5 to 800° (Baubigny, *C. r.*, 1897, **124**, 499, and 560). It is a white powder, turning yellow upon heating and white again upon cooling; melts at a full red heat, becoming crystalline upon cooling; slightly soluble in water, fairly soluble in glycerine (5*b*). Antimonous oxide sometimes acts as an acid, $Sb_2O_3 + 2NaOH = 2NaSbO_2 + H_2O$; but more commonly as a base. Ortho and pyro antimonous acids are known in the free state. The meta compound exists only in its salts (*D.*, **2**, 1, 198). (*b*) Diantimony tetroxide, Sb_2O_4, is formed by heating Sb°, Sb_2S_3, Sb_2O_3, or Sb_2O_5 in the air at a dull red heat for a long time. The antimony in this compound is probably not a tetrad, but a chemical union of the triad and pentad: $2Sb_2O_4 = 2Sb'''Sb^{V}O_4 = Sb_2O_3.Sb_2O_5$. It is found native as antimony ochre. (*c*) Antimonic oxide, Sb_2O_5, is formed by treating Sb°, Sb_2O_3 or Sb_2O_4 with concentrated nitric acid. When heated to 300° it loses oxygen, forming Sb_2O_4 (Geuther, *J. pr.*, 1871, (2), **4**, 438). It is a citron-yellow powder, insoluble in water but reddening moist blue litmus paper. Antimonic acid exists in the three * forms, analogous to the arsenic and phosphoric acids.

* Beilstein and Blaese (*C. C.*, 1889, 803) have prepared a number of antimonates and conclude that the acid is always the meta, $H\,SbO_3$.

i. e., ortho, meta and pyro (Geuther, *l. c.*, and Conrad, *C. N.*, 1879, **40**, 198). The ortho acid, H_3SbO_4, is formed by the decomposition of the pentachloride with water and washing until the chloride is all removed (Conrad, *l. c.*, and Daubrawa, *A.*, 1877, **186**, 110). The most of the antimonates formed in the wet way by precipitation from the acid solution of antimonic chloride are the ortho antimonates. By heating the ortho acid to 200° the meta acid, $HSbO_3$, is formed. Strong ignition of Sb_2O_3 with potassium nitrate and extraction with water gives the potassium metantimonate, $KSbO_3$, and by adding nitric acid to a solution of this salt the free acid is formed. The ortho acid dried at 100° gives the pyro acid: $2H_3SbO_4 = H_4Sb_2O_7 + H_2O$ (Conrad, *l. c.*), which upon further heating to 200° gives the meta acid. The pyroantimonic acid forms two series of salts, $M_4Sb_2O_7$ and $M_2H_3Sb_2O_7$. The sodium salt $Na_2H_2Sb_2O_7$ is insoluble in water and is formed in the quantitative estimation of antimony (9), and also in a method for the detection of sodium (§206, 6*g*). For the latter the soluble potassium salt $K_2H_2Sb_2O_7$ is used as the reagent. It is prepared by fusing antimonic acid with a large excess of potassium hydroxide; then dissolving, filtering, evaporating and digesting hot, in syrupy solution, with a large excess of potassium hydroxide, best in a silver dish, decanting the alkaline liquor, and stirring the residue to granulate, dry. This reagent must be kept dry, and dissolved when required for use; inasmuch as, in solution, it changes to the tetrapotassium pyroantimonate, $K_4Sb_2O_7$, which does not precipitate sodium. The reagent is, of course, not applicable in acid solutions. The reaction is as follows: $K_2H_2Sb_2O_7 + 2NaCl = Na_2H_2Sb_2O_7 + 2KCl$ (§11).

The ortho acid, H_3SbO_4, is sparingly soluble in water, easily soluble in KOH, but insoluble in NaOH. The meta acid, $HSbO_3$, is sparingly soluble in water, easily soluble in both the fixed alkalis; the pyro acid, $H_4Sb_2O_7$, is sparingly (more easily than the meta) soluble in water; the normal fixed alkali salts, $R_4Sb_2O_7$, are soluble in water, also the acid potassium salt, $K_2H_2Sb_2O_7$, but not the corresponding sodium salt, $Na_2H_2Sb_2O_7$.

5. **Solubilities.**—*a.—Metal.*—Antimony is attacked but not dissolved by nitric acid, forming Sb_2O_3 (*a*) or Sb_2O_5 (*b*), depending upon the amount and degree of concentration of the acid; it is slowly dissolved by hot concentrated sulphuric acid, evolving SO_2 and forming $Sb_2(SO_4)_3$ (*c*); it is insoluble in HCl out of contact with the air, but the presence of moist air causes the oxidation of a small amount of the metal to Sb_2O_3, which is dissolved in the acid without evolution of hydrogen (Ditte and Metzner, *A. Ch.*, 1896, (6), **29**, 389).

The best solvent for antimony is nitric acid, followed by hydrochloric acid or nitrohydrochloric acid containing only a small amount of nitric acid. Antimonous chloride, $SbCl_3$, is at first formed (*d*), but if sufficient nitric acid be present this is rapidly changed to antimonic chloride, $SbCl_5$ (*e*). If, however, too much nitric acid be present, the corresponding oxides (not readily soluble in nitric acid) are precipitated (6*c*). The halogens readily attack the metal forming at first the corresponding trihalogen compounds (*d*). Chlorine and bromine (gas) unite with the production of light, and if the halogen be in excess, the pentad chloride (*e*) or bromide is formed (Berthelot and Petit, *A. Ch.*, 1891, (6), **18**, 65). The pentiodide, SbI_5, does not appear to exist (Mac Ivor, *J. C.*, 1876, **29**, 328).

(*a*) $2Sb + 2HNO_3 = Sb_2O_3 + 2NO + H_2O$

(*b*) $6Sb + 10HNO_3 = 3Sb_2O_5 + 10NO + 5H_2O$

(*c*) $2Sb + 6H_2SO_4 = Sb_2(SO_4)_3 + 3SO_2 + 6H_2O$

(*d*) $2Sb + 3Cl_2 = 2SbCl_3$

(*e*) $SbCl_3 + Cl_2 = SbCl_5$

b.—Oxides.—Antimonous oxide, Sb_2O_3, is soluble in 55,000 parts of water at 15° and in 10,000 parts at 100° (Schulze, *J. Pr.*, 1883, (2), **27**, 320); insoluble in alcohol; soluble in hydrochloric (*a*), sulphuric and tartaric (*b*) acids with formation of the corresponding salts. The dry ignited oxide is scarcely at all soluble in nitric acid; the moist, freshly precipitated oxide, on the other hand, dissolves readily in the dilute or concentrated acid, be it hot or cold. Under certain conditions of concentration a portion of the antimony precipitates out upon standing as a white crystalline precipitate. It is soluble in the fixed

alkali hydroxides with formation of metantimonites (*c*) (Terreil, *A. Ch.*, 1866, (4), **7**, 350). Fixed alkali carbonates dissolve a small amount of the oxide with the probable formation of some antimonite (*d*) (Schneider, *Pogg.*, 1859, **108**, 407). It is fairly soluble in glycerine (Kohler, *Dingl.*, 1885, **258**, 520).

(*a*) $Sb_2O_3 + 6HCl = 2SbCl_3 + 3H_2O$

(*b*) $Sb_2O_3 + H_2C_4H_4O_6 = (SbO)_2C_4H_4O_6 + H_2O$

(*c*) $Sb_2O_3 + 2KOH = 2KSbO_2 + H_2O$

(*d*) $Sb_2O_3 + Na_2CO_3 = 2NaSbO_2 + CO_2$

Antimony tetroxide, Sb_2O_4, is insoluble in water, slowly dissolved by hot concentrated hydrochloric acid. Antimonic oxide, Sb_2O_5, is insoluble in water; soluble in hydrochloric and tartaric acids without reduction; hydriodic acid dissolves it as antimonous iodide with liberation of iodine (*6f*); slowly soluble in concentrated fixed alkalis; soluble in alkaline solution of glycerine (Kohler, *J. C.*, 1886, **50**, 428). The hydrated oxides of antimony (acids) have essentially the same solubilities as the oxides (4).

c.—Salts.—Antimonous chloride, $SbCl_3$, is very *deliquescent*, decomposed by pure water, forming a basic salt; soluble in water strongly acidulated with an inorganic acid, or tartaric, citric, or oxalic acids (*6b*), but not when acidulated with acetic acid; it is also soluble in concentrated solutions of the chlorides of the alkalis and of the alkaline earths (Atkinson, *C. N.*, 1883, **47**, 175). The bromide and iodide are *deliquescent* and require moderately concentrated acid to keep them in solution. The sulphate, $Sb_2(SO_4)_3$, dissolves in moderately concentrated sulphuric acid. Antimonous tartrate and the potassium antimonous tartrate (tartar-emetic) are soluble in water without acidulation; the latter is soluble in glycerine and insoluble in alcohol. The trichloride, bromide and iodide are soluble in hot CS_2; the chloride and bromide are soluble in alcohol without decomposition, but the iodide is partially decomposed by alcohol or ether (Mac Ivor, *J. C.*, 1876, **29**, 328).

The pentachloride, $SbCl_5$, is a liquid, very readily combining with a small amount of water to form crystals containing one or four molecules of water. The addition of more water decomposes the salt forming the basic salt; if, however, a few drops of HCl have been added first, any desired amount of water (if added at one time) may be added without causing a precipitation of the basic salt. If after acidulation water be added slowly, the basic salt will soon be precipitated.

Antimonous sulphide, Sb_2S_3, is readily soluble in K_2S, and on evaporation large yellow transparent crystals of $K_4Sb_2S_5$ are obtained (*a*) (Ditte, *C. r.*, 1886, **102**, 168 and 212). It is soluble in moderately concentrated HCl with evolution of H_2S (*b*); slowly decomposed by boiling with water into Sb_2O_3 and H_2S (*c*); and on boiling with NH_4Cl into $SbCl_3$ and $(NH_4)_2S$ (de Clermont, *C. r.*, 1879, **88**, 972). Dilute H_2SO_4 is almost without action, dilute HNO_3 gives Sb_2O_3 (*d*). Sparingly soluble in hot NH_4OH solution, soluble in the fixed alkalis (on fusion or boiling) (*e*); insoluble in $(NH_4)_2CO_3$ (distinction from arsenic); insoluble in the fixed alkali carbonates in the cold but on warming they effect complete solution (*f*) (distinction from tin); very sparingly soluble in normal ammonium sulphide; readily soluble in yellow ammonium sulphide with oxidation (*g*) (*6e*). The pentasulphide, Sb_2S_5, is insoluble in water; soluble in the alkali sulphides (*h*), and in the fixed alkali carbonates and hydroxides; insoluble in ammonium carbonate and sparingly soluble in ammonium hydroxide, more readily when warmed (*D.*, **2**, 1, 217). On boiling with water it slowly decomposes into Sb_2O_3,

H_2S and S (Mitscherlich, *J. pr.*, 1840, **19**, 455). Hydrochloric acid on warming dissolves it as $SbCl_3$ (*i*):

(*a*) $Sb_2S_3 + 2K_2S = K_4Sb_2S_5$
(*b*) $Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S$
(*c*) $Sb_2S_3 + 3H_2O = Sb_2O_3 + 3H_2S$
(*d*) $2Sb_2S_3 + 4HNO_3 = 2Sb_2O_3 + 3S_2 + 4NO + 2H_2O$
(*e*) $2Sb_2S_3 + 4KOH = 3KSbS_2 + KSbO_2 + 2H_2O$
(*f*) $2Sb_2S_3 + 2Na_2CO_3 = 3NaSbS_2 + NaSbO_2 + 2CO_2$
(*g*) $2Sb_2S_3 + 6(NH_4)_2S_2 = 4(NH_4)_3SbS_4 + S_2$
(*h*) $Sb_2S_5 + 3(NH_4)_2S = 2(NH_4)_3SbS_4$
(*i*) $Sb_2S_5 + 6HCl = 2SbCl_3 + 3H_2S + S_2$

*d.—Water.**—With the exception of the compounds of antimony with some organic acids, as tartaric and citric, all salts of antimony are decomposed by pure **WATER.** For this reason it will be seen that water is a very important reagent in the analysis of antimony salts. The salts with inorganic acids all require the presence of some free acid (not acetic) to keep them in solution. If the acid be tartaric the further addition of water causes no precipitation of the antimony salt. Water decomposes the inorganic acid solutions precipitating the basic salt, setting more acid free which dissolves a portion of the basic salt. The addition of more water causes a further precipitation and at the same time dilutes the acid so that upon the addition of a sufficient amount of water a nearly complete precipitation may be obtained. If the precipitate of the basic salt be washed with water the acid is gradually displaced, leaving finally the antimony as oxide.

With solutions of antimonous chloride the basic salt precipitated is white antimonous oxychloride, $Sb_4Cl_2O_5$, "Powder of Algaroth," soluble in tartaric acid (distinction from bismuth, §**76**, 5*d*) (Mac Ivor, *C. N.*, 1875, **32**, 229), $4SbCl_3 + 5H_2O = Sb_4Cl_2O_5 + 10HCl$. The basic salt repeatedly washed with water is slowly (rapidly if alkali carbonate be used) changed to the oxide, Sb_2O_3 (Malaguti, *J. pr.*, 1835, **6**, 253), $Sb_4Cl_2O_5 + H_2O = 2Sb_2O_3 + 2HCl$. With antimonic chloride, $SbCl_5$, the basic salt is $SbOCl_3$; $SbCl_5 + H_2O = SbOCl_3 + 2HCl$ (Williams, *C. N.*, 1871, **24**, 224).

Solutions of the tartrates of antimony and of antimony and potassium are not precipitated on the addition of water; and antimonous chloride

*The acidity of water solutions of certain salts having a weak base and the alkalinity of others containing a weak acid is due to a partial decomposition (hydrolysis) of the salt by the ions of the water, H^+ and OH^-, forming again the original acid and base. Na_2CO_3, for instance, is split up into the weak non-dissociated H_2CO_3 and the strongly-dissociated **NaOH**, whose **OH** ions give the "alkaline reaction." $FeCl_3$ in water forms soluble colloidal $Fe(OH)_3$, which may be separated by dialysis from the free **HCl** resulting or precipitated by addition of a neutral salt, as **NaCl**, to the dilute solution; **KCN** gives alkaline **KOH** and non dissociated **HCN**, readily detected by its odor. In other cases precipitation is caused, as in the treatment of bismuth or antimony solutions with water or on heating Na_2ZnO_2 solution, hydrolysis in general being increased by raising the temperature. The action of water on soap belongs to this class.

dissolved in excess of tartaric or citric acid solution is not precipitated on addition of water.

6. **Reactions.**—*a.*—The **alkali hydroxides** and **carbonates** precipitate from acidulated solutions of inorganic antimonous salts, antimonous oxide.* Sb_2O_3 (*a*) (Rose, *Pogg.*, 1825, **3**, 441), white, bulky, readily becoming crystalline on boiling; sparingly soluble in water (*5b*), readily soluble in excess of the *fixed alkalis*, forming a metantimonite (*b*) (Terreil, *A. Ch.*, 1866, (4), **7**, 350); slowly soluble in a strong excess of a hot solution of the fixed alkali carbonate (*c*) (distinction from tin); insoluble in ammonium hydroxide or ammonium carbonate. The freshly precipitated oxide is readily soluble in acids (not in acetic acid). If the alkaline solution of the antimony be carefully neutralized with an acid (not tartaric or citric) the oxide is precipitated (*d*) and at once dissolved by further addition of acid. The presence of tartaric or citric acids prevents the precipitation of the oxide by means of the alkalis or alkali carbonates.

Antimonous oxide acts as a feebly acidic anyhdride toward alkalis, with which it combines, dissolving in their solutions and forming antimonites, which are found to be monobasic, so far as capable of isolation. Sodium antimonite, $NaSbO_2$, is the most stable and the least soluble in water: potassium antimonite, $KSbO_2$, is freely soluble in dilute potassium hydroxide solution, but decomposed by pure water. By long standing (24 hours), a portion of the antimonous oxide deposits from the alkaline solution, and the presence of alkali hydrogen carbonates causes a nearly complete separation of that oxide (*c*).

(*a*) $2SbCl_3 + 6KOH = Sb_2O_3 + 6KCl + 3H_2O$

$2SbCl_3 + 3Na_2CO_3 = Sb_2O_3 + 6NaCl + 3CO_2$

(*b*) $Sb_2O_3 + 2KOH = 2KSbO_2 + H_2O$

or $SbCl_3 + 4KOH = KSbO_2 + 3KCl + 2H_2O$

(*c*) $Sb_2O_3 + Na_2CO_3 = 2NaSbO_2 + CO_2$

(*d*) $2KSbO_2 + 2HCl = Sb_2O_3 + 2KCl + H_2O$

(*e*) $2NaSbO_2 + 2NaHCO_3 = Sb_2O_3 + 2Na_2CO_3 + H_2O$

Antimonic salts are precipitated under the same conditions as the antimonous salts. The freshly formed precipitate is the orthoantimonic acid, $H_3SbO_4 = SbO(OH)_3 = Sb_2O_5,3H_2O$ (*a*) (Conrad, *C. N.*, 1879, **40**, 198); insoluble in ammonium hydroxide or carbonate; soluble, more readily upon warming, in excess of the fixed alkali hydroxides and carbonates as metantimonate (*b*).

(*a*) $SbCl_5 + 5KOH = SbO(OH)_3 + 5KCl + H_2O$

(*b*) $SbO(OH)_3 + KOH = KSbO_3 + 2H_2O$

b.—The freshly precipitated antimonous oxide is soluble in **oxalic acid**, but (in absence of tartaric acid) the antimony soon slowly but completely separates out as a white crystalline precipitate; unless an alkali oxalate be present, when the soluble double oxalate is formed. The precipitate of antimony oxalate dissolves upon the further addition of hydrochloric acid. Freshly precipitated antimonic oxide dissolves readily in oxalic acid and does not separate out upon standing. **Acetic acid** precipitates the solutions of antimony salts if tartaric acid be absent. **Potassium cyanide** gives a white precipitate with antimonous salts soluble in excess of the cyanides.

With **potassium ferrocyanide** antimonous chloride (not tartrate) gives a white precipitate, soluble in hydrochloric acid (distinction from tin), or fixed alkali hydroxides (Warren, *C. N.*, 1888, **57**, 124). **Potassium ferricyanide** is reduced to ferrocyanide by antimonous salts in alkaline solution (Baumann, *Z. angew.*, 1892, 117).

c.—From the solutions of the fixed alkali antimonites or antimonates the oxides or hydrated oxides (acids) are precipitated upon neutralization with **nitric acid** (or other inorganic acids); the freshly formed precipitates readily

* Menschutkin (page 185) says the precipitate formed by the action of alkalis upon antimonous salts is the meta acid, $HSbO_2$.

dissolving in an excess of the acid. Antimonous nitrate is very unstable and the antimonic nitrate is not known to exist. It is quite probable that these solutions in nitric acid are merely solutions of some of the hydrated oxides (acids).

d. Compounds of antimony with the acids of **phosphorus** are not known, (Na_2HPO_4 does not precipitate antimony salts, separation from tin, §71, 6*d*).

e. **Hydrogen sulphide** precipitates, from acid * solutions of antimonous salts, *antimonous sulphide* (*a*), Sb_2S_3, orange-red; in neutral solutions (tartrates) the precipitation is incomplete. In strong fixed alkali solutions (6*a*) the precipitation is prevented, or rather the sulphide first formed (*b*) is at once dissolved in the excess of the fixed alkali (*c*), sparingly in NH_4OH. The alkali sulphides give the same precipitate sparingly soluble in normal ammonium sulphide, readily soluble in the fixed alkali sulphides (*d*) and in yellow ammonium sulphide (*e*). Antimonous sulphide is slowly decomposed by boiling water (*f*); insoluble in ammonium carbonate (distinction from **As**); slowly soluble in boiling solution of the fixed alkali carbonates (*g*) (distinction from **Sn**); soluble in hot moderately concentrated hydrochloric acid (*h*) (distinction from arsenic). The alkaline solutions of antimonous sulphide are oxidized upon standing by the oxygen of the air or rapidly in the presence of sulphur (*e*); from the alkaline solutions hydrochloric acid precipitates the antimony as trisulphide, penta sulphide or a mixture of these, depending upon the degree of oxidation (*i*).

(*a*) $2SbCl_3 + 3H_2S = Sb_2S_3 + 6HCl$

(*b*) $2KSbO_2 + 3H_2S = Sb_2S_3 + 2KOH + 2H_2O$

(*c*) $2Sb_2S_3 + 4KOH = 3KSbS_2 + KSbO_2 + 2H_2O$

(*d*) $Sb_2S_3 + K_2S = 2KSbS_2$

(*e*) $2Sb_2S_3 + 6(NH_4)_2S_2 = 4(NH_4)_3SbS_4 + S_2$

(*f*) $Sb_2S_3 + 3H_2O = Sb_2O_3 + 3H_2S$

(*g*) $2Sb_2S_3 + 2K_2CO_3 = 3KSbS_2 + KSbO_2 + 2CO_2$

(*h*) $Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S$

(*i*) $3KSbS_2 + KSbO_2 + 4HCl = 2Sb_2S_3 + 4KCl + 2H_2O$

or $2(NH_4)_3SbS_4 + 6HCl = Sb_2S_5 + 6NH_4Cl + 3H_2S$

Hydrosulphuric acid † and alkali **sulphides** precipitate (under like conditions as for antimonous salts), from solutions of antimonic salts, *antimonic sulphide*, Sb_2S_5, orange, having the same solubilities as the tri-sulphide. The alkaline solution of the sulphide consists chiefly of the ortho-thioantimonate instead of the meta, as in antimonous compounds. $Sb_2S_5 + 3K_2S = 2K_3SbS_4$; $4Sb_2S_5 + 18KOH = 5K_3SbS_4 + 3KSbO_3 + 9H_2O$. When dissolved in **HCl** the penta-sulphide is reduced to $SbCl_3$ with liberation of sulphur, $Sb_2S_5 + 6HCl = 2SbCl_3 + 3H_2S + S_2$.

* According to Loviton (*J. C.*, 1888, **54**, 992) the precipitation takes place in the presence of quite strong hydrochloric acid (one to one) separation from tin, which is precipitated only when three or more parts of water are present to one of the acid. See also Noyes and Bray, *J. Am. Soc.*, **29**, 137 (1917).

† In order to precipitate pure *antimonic sulphide*, the solution of the antimonic salt must be cold, and the **hydrogen sulphide** added rapidly. If the solution be warmed or the hydrogen sulphide added slowly more or less antimonous sulphide is precipitated (Bősek, *J. C.*, 1895, **67**, 515).

All salts of antimony when warmed with **sodium thiosulphate, $Na_2S_2O_3$**, are precipitated as the sulphide (separation of arsenic and antimony). $2SbCl_3 + 3Na_2S_2O_3 + 3H_2O = Sb_2S_3 + 3Na_2SO_4 + 6HCl$. **Sulphurous acid** reduces antimonic salts to antimonous salts (Knorre, *Z. angew.*, 1888, 155). *Sulphates* of antimony are not prepared by precipitation, but by boiling the oxides with strong **sulphuric acid.** They dissolve only in very strongly acidulated water.

f.—Antimony occurs most frequently for analysis as the *chlorides;* it is therefore important that the student familiarize himself with the deportment of these salts with the various reagents, used in qualitative analysis. The most important of the properties have been discussed under 5*a*, *b*, *c*, *d*. **Hydrochloric acid,** or any other inorganic acid, carefully added to a solution of antimony salts in the fixed alkalis will precipitate the corresponding oxide or hydrated oxide, soluble upon further addition of the acid. **Potassium iodide** added to antimonous chloride solution, not too strongly acid, gives a yellow precipitate of *antimonous iodide*, soluble in hydrochloric acid. The precipitation does not take place in the presence of tartaric or oxalic acids. **Hydriodic acid** (or potassium iodide in acidulated solutions) added to solutions of antimonic salts causes a reduction of the antimony to an *antimonous salt* with liberation of *iodine* (distinction from Sn^{IV}: $SbCl_5 + 2HI = SbCl_3 + 2HCl + I_2$. The iodine may be detected by heating and obtaining the violet vapors, or by adding carbon disulphide and shaking. It should be remembered that the solution to be tested must be acid, for in alkaline solutions the reverse action takes place, iodine oxidizing antimonous salts to antimonic salts: $SbCl_3 + 8KOH + I_2 = K_3SbO_4 + 2KI + 3KCl + 4H_2O$ (Weller, *A.*, 1882, **213**, 364). Also the absence of other oxidizing agents which liberate iodine from hydriodic acid must be assured.

g.—If antimony and arsenic compounds occurring together are strongly oxidized with nitric acid there is danger that the insoluble precipitate of antimonic oxide may contain arsenic, as antimonic arsenate, insoluble (Menschutkin). **Stannous chloride** reduces antimonic compounds to the antimonous condition, but in no case causes a precipitation of the metal (distinction from arsenic).

h.—Antimonous salts in acid, neutral or alkaline solution, rapidly reduce solutions of **chromates** to chromic compounds. Acid solutions of antimonous salts reduce solutions of **manganates** and **permanganates** to manganous salts; with alkaline solutions to manganese dioxide. These reactions are capable of quantitative application in absence of other reducing agents. The antimony is oxidized to the *antimonic* condition (9 and 10).

i.—An antimonous compound when evaporated on a water bath with an ammoniacal solution of **silver nitrate** gives a black precipitate (Bunsen, *A.*, 1855, **106**, 1). A solution of an antimonous compound in fixed alkali when treated with a solution of silver nitrate gives a heavy black precipitate of metallic silver, insoluble in ammonium hydroxide, and thus separated from the precipitated silver oxide. If instead of a water solution of silver nitrate, a solution with great excess of ammonium hydroxide (one to sixteen) be added, no precipitation occurs in the cold (distinction from Sn''); nor upon heating until the excess of ammonia has been driven off. Antimonates with silver nitrate give a white precipitate of silver antimonate, soluble in ammonium hydroxide.

j.—**Stibine.**—By the action of zinc and sulphuric or hydrochloric acid all compounds of antimony are first reduced to the metallic state. The formation of stibine is a secondary reaction and requires the moderately rapid generation of hydrogen in acid solution. If a few drops of a solution of an antimony salt, acidulated with hydrochloric acid, be placed upon a platinum foil and a small piece of zinc be added, the antimony is immediately deposited as a black stain or coating adhering firmly to the platinum; $2SbCl_3 + 3Zn = 2Sb + 3ZnCl_2$. In this test tin, if present, deposits as a loose spongy mass, while arsenic, if present, does not adhere so firmly to the platinum as the antimony. In the presence of arsenic this test should be applied with caution under a hood as a portion of the arsenic is almost immediately evolved as arsine (§69, 6′*b*).

If hydrogen be generated more abundantly than in the operation above mentioned, by zinc and dilute sulphuric or hydrochloric acid, the gaseous antimony hydride, *stibine*, SbH_3, is obtained for examination. For comparison with arsine and details of manipulation see "Marsh's Test" under arsenic (§69, 6′*a*):

$$Sb_2O_3 + 6Zn + 6H_2SO_4 = 6ZnSO_4 + 3H_2O + 2SbH_3$$
$$SbCl_3 + 3Zn + 3HCl = 3ZnCl_2 + SbH_3$$

Stibine is a colorless, odorless gas, not nearly so poisonous as arsine. It burns with a luminous and faintly bluish-green flame, dissipating vapors of antimonous oxide and of water (*a*); or depositing antimony on cold porcelain held in the flame, as a lusterless brownish-black spot (*b*). The gas is also decomposed by passing through a small glass tube heated to low redness (*c*), forming a lustrous ring or mirror in the tube. The stibine is decomposed more readily by heat than the arsine and the mirror is deposited on both sides of the heated portion of the glass tube. The spots and mirror of antimony are compared with those of arsenic in §69, 6′*c*. The antimony in stibine is deposited as the metal when the gas is passed into a concentrated solution of fixed alkali hydroxide or when it is passed through a U tube filled with solid caustic potash or soda-lime (distinction and separation from arsenic).

(*a*) $2SbH_3 + 3O_2 = Sb_2O_3 + 3H_2O$
(*b*) $4SbH_3 + 3O_2 = 4Sb + 6H_2O$
(*c*) $2SbH_3 = 2Sb + 3H_2$

When the **antimony hydride** (stibine) is passed into a solution of **silver nitrate,** the **silver** is reduced, leaving the antimony with the silver, as *antimonous argentide,* $SbAg_3$, a black precipitate, distinction from arsenic, which enters into solution (§69, 6′*a* and *b*); $SbH_3 + 3AgNO_3 = SbAg_3 + 3HNO_3$. The precipitate should be filtered and washed free from undecomposed silver salt (and arsenous acid, if that be present), and dissolved with dilute hydrochloric acid (**HCl** does not dissolve uncombined anti-

mony, 5*a*): $SbAg_3 + 6HCl = SbCl_3 + 3AgCl + 3H_2$. The solution consists of antimonous chloride, leaving silver chloride as a precipitate. However, in the excess of hydrochloric acid used a small portion of the silver chloride may be dissolved (§**59**, 5*c*), interfering with the final test for the antimony. If this be the case the silver should be removed by a drop of potassium iodide (8).

Stibine is not evolved by the action of strong **KOH** upon zinc or aluminum, nor by sodium amalgam in neutral or alkaline solution (distinction from triad arsenic); the antimony is precipitated as the metal (Fleitmann, *J. C.*, 1852, **4**, 329). Stibine is slowly oxidized by sulphur to Sb_2S_3 in the sunlight at ordinary temperature and rapidly when the sulphur (in a U tube mixed with glass wool) is heated to 100°. The reaction takes place according to the following equation: $2SbH_3 + 3S_2 = Sb_2S_3 + 3H_2S$ (Jones, *J. C.*, 1876, **29**, 645).

7. **Ignition.**—By ignition in the absence of reducing agents, antimonic acid and anhydride are reduced to antimonous antimonate, $Sb_2O_4.Sb_2O_3$, or Sb_2O_4 ($Sb'''Sb^vO_4$), a compound unchanged at a dull red heat, but when heated to 800° this oxide is further reduced to antimonous oxide (4*b*).

The antimonates of the fixed alkali metals are not vaporized or decomposed when ignited in the absence of reducing agents; hence, by fusion in the crucible with sodium carbonate and oxidizing agents, *i. e.*, with sodium nitrate and carbonate, the compounds of antimony are converted into non-volatile sodium pyroantimonate, $Na_4Sb_2O_7$, and arsenic compounds if present are at the same time changed to sodium orthoarsenate, Na_3AsO_4. If now the fused mass be digested and disintegrated in cold water and filtered, the antimonate is separated as a residue, $Na_2H_2Sb_2O_7$ (4*c*), while the arsenate remains in solution with the excess of alkali. The operation is much more satisfactory when the arsenic and antimony are previously fully oxidized—as by digestion with nitric acid—as the oxidation by fusion in the crucible is not effected soon enough to retain all the arsenic or antimony which may be in the state of lower oxides, sulphides, etc. If compounds of tin are present in the operation—and if the fusion is not done with excess of heat, so as to convert sodium nitrite to caustic soda and form the soluble sodium stannate—the tin will be left as stannic oxide, SnO_2, in the residue with the $Na_2H_2Sb_2O_7$. But if sodium hydroxide is added in the operation, the tin is separated as stannate in solution with the arsenic (Meyer, *J. C.*, 1849, **1**, 388).

All compounds of antimony are completely reduced in the dry way on charcoal with sodium carbonate, more rapidly with potassium cyanide; the metal fusing to a brittle globule. The reduced metal rapidly oxidizes, the white antimonous oxide rising in fumes, and making a crystalline deposit on the support. If now ammonium sulphide be added to this white sublimate, an orange precipitate is a sure indication of the presence of antimony (Johnstone, *C. N.*, 1883, **58**, 296). The same white oxide is formed on heating antimony or its sulphides in a glass tube, through which air is allowed to pass.

8. **Detection.**—Antimony is precipitated, from the solution acidulated with hydrochloric acid, in the second group by **hydrosulphuric acid** as the sulphide (6*e*). By its solution in **yellow ammonium sulphide** * it is separated from **Hg**, **Pb**, **Bi**, **Cu**, and **Cd**. In the Marsh apparatus the antimony is precipitated on the **Zn** as the metal, a portion being still further reduced to stibine. By passing the gases, *stibine* and *arsine*, into $AgNO_3$ solution, the antimony is precipitated as $SbAg_3$, *antimony argentide*, sepa-

* Antimony as sulphide solution in potassium sulphide may be detected electrolytically, being deposited as **Sb°**. Delicate to one part in 1,500,000 (Kohn, *J. Soc. Ind.*, 1891, **10**, 327).

rating it from the arsenic which is oxidized and passes into solution as arsenous acid. The $SbAg_3$ is dissolved in **HCl** and the presence of the antimony is confirmed by the precipitation of the orange colored sulphide with H_2S. Study text at 6 and §84 to §89. For distinction between Sb^V and Sb''' see §89, 7.

9. **Estimation.**—(*1*) Tartaric acid and water are added to $SbCl_3$, which is then precipitated by H_2S as Sb_2S_3, and after washing on a weighed Gooch filter, it is heated to 230° in a stream of CO_2, in order to exclude oxygen, and weighed. (*2*) Antimonous oxide, sulphide, or any oxysalt of antimony is first boiled with fuming nitric acid, which converts it into Sb_2O_5, and then by ignition it is reduced to Sb_2O_4, and weighed as such. (*3*) The trichloride is precipitated by gallic acid, and weighed after drying at 100°. (*4*) In the presence of tin and lead oxidize the hydrochloric acid solution of the salts with $KClO_3$ (the tin must be present as Sn^{IV}) and distil in a current of **HCl**. The stannic and antimony chlorides are volatile (separation from lead). To the distillate add metallic iron, obtaining stannous chloride and metallic antimony; filter and wash (separation from tin). Fuse the precipitate with sodium nitrate and sodium carbonate, digest the fused mass with cold water, filter, wash, dry and weigh as $Na_2H_2Sb_2O_7$ (7) (Tookey, *J. C.*, 1862, **15**, 462; and Thiele, *A.*, 1894, **263**, 361). (*5*) For estimation of antimony and separation from arsenic and tin by the use of oxalic acid, see Lessen (*Z.*, 1888, **27**, 218) and Clarke (*C. N.*, 1870, **21**, 124). (*6*) Volumetrically. The antimony compound is converted into stibine (6*j*) and the gas passed into standard silver nitrate solution. The solution is filtered and the excess of silver nitrate is titrated with standard sodium chloride. If arsenic be present it must also be estimated (§69, 9 (*15*)), and the true amount of antimony present computed from the two determinations (Houzeau, *J. C.*, 1873, **26**, 407). (*7*) Sb''' is oxidized to Sb^V in presence of $NaHCO_3$ by a standard solution of iodine. The end of the reaction is shown by the blue color given to starch. (*8*) Sb''' is oxidized by $KClO_3$ in strong **HCl** solution to $SbCl_5$. **KI** is added, which reduces the Sb_V to Sb''' with the liberation of I_2, which is titrated with $Na_2S_2O_3$ solution. (*9*) Sb''' is oxidized to Sb^V in presence of $H_2C_4H_4O_6$ by $KMnO_4$. (*10*) Sb''' is oxidized to Sb^V by $K_2Cr_2O_7$, and the excess of $K_2Cr_2O_7$ used is determined by a standard solution of $FeSO_4$, $K_3Fe(CN)_6$ being used to show the end of the reaction. (*11*) The antimony as the triad salt is treated with an excess of standard $K_3Fe(CN)_6$; the excess of which is estimated in a gas apparatus with H_2O_2 (Baumann, *Z. angew.*, 1892, 117).

10. **Oxidation.**—Stibine, SbH_3, is decomposed by heat alone into antimony and hydrogen (6*j*). By burning in the air it is oxidized to Sb_2O_3 and H_2O. Passed into a solution of silver nitrate, $SbAg_3$ is produced, or passed into a solution of antimonous chloride or potassium hydroxide, sp. gr. 1.25, metallic antimony is produced. Excess of chlorine, bromine, or nitric acid in presence of water oxidizes it to Sb^V; but if the SbH_3 be in excess metallic antimony is precipitated. With excess of iodine in presence of water Sb''' is produced; if the stibine be in excess metallic antimony. Metallic antimony is oxidized by nitric acid, chlorine or bromine to Sb''' or Sb^V, depending upon the amount of these reagents and the temperature. Iodine oxidizes the metal to Sb''' only, except in alkaline mixtures when Sb^V is formed.

Antimonous compounds are oxidized to antimonic compounds by **Cl**, **Br**, HNO_3, $K_2Cr_2O_7$, and $KMnO_4$; by silver oxide in presence of the fixed alkalis (6*i*); by gold chloride in hydrochloric acid solution, gold being

deposited as a yellow precipitate (§73, 10). The antimony is precipitated as Sb_2O_5 unless sufficient acid be present to dissolve the oxide: $4AuCl_3 + 3Sb_2O_3 + 6H_2O = 4Au + 3Sb_2O_5 + 12HCl$.

Antimonic compounds are reduced to antimonous compounds by **HI** (6*f*) and by $SnCl_2$ (§69 and §71, 10); the antimony not being further reduced (distinction from **As**). Antimonic and antimonous compounds are reduced to the metallic state by **Pb**, **Sn**, **Bi**, **Cu**, **Cd**, **Fe**, **Zn**, and **Mg**; but in the presence of dilute acids and metals which evolve hydrogen the antimony is still further reduced to stibine. Iron alone or in the presence of platinum (iron platinum wire couple) precipitates the antimony from acid solutions as **Sb°**; 0.000012 grams can be detected (Rideal, *C. N.*, 1885, **51**, 292).

Sodium amalgam with dilute sulphuric acid evolves stibine from all antimony solutions (Van Bylert, *B.*, 1890, **23**, 2968) but the generation of hydrogen in alkaline solution, *i. e.*, **Zn + KOH**, causes the reduction of the antimony salt to the metal only, in no case evolving stibine.

§71. Tin (Stannum). Sn = 118.7. Valence two and four.

1. **Properties.**—*Specific gravity*, 7.2984 (Rammelsberg, *B.*, 1870, **3**, 724); *melting point*, 231.68° (Callendar and Griffiths, *C. N.*, 1891, **63**, 2). Boils at 2275° (Greenwood, *Proc. Roy. Soc.*, **82**, 396, 1908). Does not distil in a vacuum at a red heat (Schuller, *J.*, 1884, 1550). Tin is a silver white metal, does not tarnish readily in pure air. At a red heat it decomposes steam with evolution of hydrogen; at a white heat it burns in the air with a dazzling white light, forming SnO_2. It is softer than gold and harder than lead, can readily be hammered or rolled into thin sheets (tinfoil); at 100° it can be drawn into wire and at 200° can be pulverized. Tin possesses a strong tendency to crystalline structure, and when bar or block tin is bent a marked decrepitation "Zinngeschrei" (Levol, *A. Ch.*, 1859, (3), **56**, 110) is noticed, due to the friction of the crystals. Block tin exposed to severe cold (winter of 1867–68, at St. Petersburg, −39°) crumbles to a grayish powder (Fritsche, *B.*, 1869, **2**, 112), considered to be an allotropic modification. This same property of crumbling is noticed in samples of tin that have been preserved several hundred years (Schertel, *J. pr.*, 1879, 2, **19**, 322). The grayish powder is an allotropic modification of tin, the transition temperature being 20° C. Tin forms alloys with many metals. Bronze consists of copper and tin, brass frequently contains from two to five per cent of tin, solder consists of lead and tin. All the easily fusible metals as Wood's metal, etc., contain tin. For many references concerning tin alloys, see Watts (**IV**, 720).

2. **Occurrence.**—The chief ore of tin is cassiterite or tinstone, a nearly pure crystallized dioxide, SnO_2; found in England, Australia, Malay Peninsula, Bolivia, Mexico, and to a very limited extent in the United States; (*D.*, **2**, 1, 643). Stannite, Cu_2FeSnS_4, is found in small quantities in various tin veins.

3. **Preparation.**—The reducing agent employed is carbon. The impure ore, SnO_2, is first roasted, which removes some of the arsenic as As_2O_3, and some of the sulphur as SO_2. Then, by washing, the soluble and some of the insoluble impurities are washed away, the heavier SnO_2 remaining. It is then fused with powdered coal, lime being introduced to form a fusible slag with the earthy impurities. It is refined by repeated fusion. Strictly pure tin is best made by treating the refined tin with HNO_3, and then reducing the oxide thus formed by fusion with charcoal; or by reducing the purified chloride.

4. **Oxides and Hydroxides.** Tin forms two stable oxides and corresponding classes of salts; stannous oxide, **SnO**, black or blue black, and stannic oxide, SnO_2, white; the latter acts both as a base, in stannic salts, and as an anhydride, in stannates. *Stannous oxide* is formed (*1*) by precipitating $SnCl_2$ with K_2CO_3, washing with boiled water in absence of air, drying at 80° or lower; then dehydrating by heating in an atmosphere of hydrogen or carbon dioxide

(Longé, *C. C.*, 1886, 34); (*2*) by melting a mixture of $SnCl_2$ and Na_2CO_3 with stirring until it becomes black, and removing the NaCl by washing (Sandal, *Phil. Mag.*, 1838, (3), **12**, 216; Böttger, *A.*, 1839, **29**, 87). *Stannous hydroxide*, $Sn(OH)_2$*, white to yellowish white, is formed by adding alkalis or alkali carbonates to stannous chloride, washing and drying at a low temperature (Ditte, *A. Ch.*, 1882, (5), **27**, 145). (§12.)

Stannic oxide exists in two forms, crystalline and amorphous. The native tinstone is nearly pure crystalline SnO_2. For preparation see Bourgeois (*C. r.*, 1887, **104**, 231) and Levy and Bourgeois (*C. r.*, 1882, **94**, 1365). Amorphous SnO_2 is formed (*1*) by heating tin in the air to a white heat; (*2*) stannic salts are precipitated by alkali carbonates, the precipitate washed and ignited; (*3*) tin is oxidized by nitric acid; (*4*) tin filings are ignited in a retort with HgO (*D.*, **2**, 1, 647). *Stannic hydroxide* or stannic acid exists in two forms: (*1*) Normal stannic acid, $SnO(OH)_2 = H_2SnO_3$, is formed when a solution of stannic chloride is precipitated by barium or calcium carbonate (Fréing, *Pogg.*, 1842, **55**, 519); if an alkali carbonate be used some alkali stannate is also formed. (*2*) Metastannic acid, $H_{10}Sn_5O_{15}$, is formed by decomposition of tin with nitric acid (Hay, *C. N.*, 1870, **22**, 298; Scott, *C. N.*, 1870, **22**, 322); insoluble in acids but changed on standing with acids to normal stannic acid, which is readily soluble in acids (*5b*). It is also formed when stannic chloride is boiled in concentrated solution with most of the alkali salts: $5SnCl_4 + 20Na_2SO_4 + 15H_2O = H_{10}Sn_5O_{15} + 20NaCl + 20NaHSO_4$, or according to Frésenius (16th edition), 271: $SnCl_4 + 4Na_2SO_4 + 4H_2O = Sn(OH)_4 + 4NaCl + 4NaHSO_4$. It is also formed together with hydrochloric acid when stannic chloride is boiled with a large excess of water.

5. **Solubilities.**—*a.—Metal.*—Tin dissolves in hydrochloric acid slowly when the acid is dilute and cold, but rapidly when hot and concentrated, stannous chloride and hydrogen being produced (*a*); in dilute sulphuric acid slowly, with separation of hydrogen (*b*), (not at all even in hot acid if more dilute than $H_2SO_4.6H_2O$ (Ditte, *A. Ch.*, (5), **27**, 145); in hot concentrated sulphuric acid rapidly, with separation of sulphurous anhydride and sulphur (*c*); nitric acid, rapidly converts it into metastannic acid, insoluble in acids (*d*); very dilute nitric acid dissolves it without evolution of gas as stannous nitrate and ammonium nitrate (*e*) (Maumené, *Bl.*, (2), **35**, 598); nitro-hydrochloric acid dissolves tin easily as stannic chloride (*f*), potassium hydroxide solution dissolves it very slowly, and by atmospheric oxidation (*g*); or, at high temperatures, with evolution of hydrogen (*h*). Bromine vapors readily attack melted tin with formation of $SnBr_4$, colorless crystals, melting point 30° (Carnelley and O'Shea, *J. C.*, 1878, **33**, 55). Dry chlorine gas attacks tin readily in the cold, producing stannic chloride as vapor or colorless liquid. The action is vigorous enough in strong chlorine to produce a flame.

(*a*) $Sn + 2HCl = SnCl_2 + H_2$

(*b*) $Sn + H_2SO_4 = SnSO_4 + H_2$

(*c*) $Sn + 2H_2SO_4 = SnSO_4 + 2H_2O + SO_2$

and then $4SnSO_4 + 2SO_2 + 4H_2SO_4 = 4Sn(SO_4)_2 + S_2 + 4H_2O$

(*d*) $15Sn + 20HNO_3 + 5H_2O = 3H_{10}Sn_5O_{15} + 20NO$

(*e*) $4Sn + 10HNO_3 = 4Sn(NO_3)_2 + 3H_2O + NH_4NO_3$

(*f*) $Sn + 2Cl_2 = SnCl_4$

(*g*) $2Sn + 4KOH + O_2 = 2K_2SnO_2 + 2H_2O$

(*h*) $Sn + 2KOH = K_2SnO_2 + H_2$

b.—Oxides.—Stannous oxide is insoluble in water, soluble in acids (Ditte, *A. Ch.*, 1882, (5), **27**, 145; Weber, *J. C.*, 1882, **42**, 1266), oxidized by nitric acid when heated, forming the insoluble metastannic acid. *Stannous hydroxide* is readily soluble in all the solvents of the oxide, and is also readily soluble in fixed alkali hydroxides. *Stannic oxide*, SnO_2, is insoluble in water; soluble with difficulty in alkalis; insoluble in acids except in concentrated H_2SO_4 (*D.*, **2**, 1, 648). Sulphur forms SnS_2 and SO_2; chlorine forms $SnCl_4$ (Weber, *Pogg.*, 1861, **112**, 619). Normal *stannic acid*, H_2SnO_3, freshly precipitated, is soluble in

* According to other authorities $Sn(OH)_2$ does not exist, but a hydrated oxide is formed, $SnO.Sn(OH)_2$ (Graham-Otto, **2**, 2, 1267; *D.*, **2**, 1, 657; Gmelin-Kraut, **3**, 107).

fixed alkali hydroxides and in acids (Ditte, *C. r.*, 1887, **104**, 172); insoluble in water and changed by hot nitric acid to the insoluble metastannic acid. *Metastannic acid*, $H_{10}Sn_5O_{15}$, is insoluble in water and acids, **HCl** changes it to metastannic chloride insoluble in the acid, but soluble in water after removal of the acid; soluble in the fixed alkalis as metastannates, which are soluble in water and precipitated by acids. Metastannic acid in contact with **HCl** is gradually changed to stannic acid (Barfoed, *J. pr.*, 1867, **101**, 368).

c.—Salts.—The sulphides and phosphates of tin are insoluble in water, also stannous oxychloride; stannous sulphate,* bromide and iodide; and stannic chloride and bromide dissolve in pure water with little or no decomposition (Personne, *C. r.*, 1862, **54**, 216; and Carnelley and O'Shea, *J. C.*, 1878, **33**, 55). Stannous chloride is soluble in less than two parts of water (Engel, *A. Ch.*, 1891, (6), **17**, 347); but more water decomposes it, unless a strong excess of acid be present: $2SnCl_2 + H_2O = SnO.SnCl_2 + 2HCl$. Pure stannic chloride is a liquid; *sp. gr.*, 2.2; boiling point, 114° (Walden, *Z. ph. Ch.*, **43**); solidifies at −33° (Besson, *C. r.*, 1889, **109**, 940). The liquid combines with water, liberating heat to form crystals of $SnCl_4.3H_2O$, which are readily soluble in excess of water (*D.*, **2**, 1, 662). Stannic chloride is completely decomposed by boiling water. The nitrates of tin are very easily decomposed by water and require free acid to keep them in solution (Weber, *J. pr.*, 1882, (2), **26**, 121; Montemartini, *Gazzetta*, 1892, **22**, 384). Stannic iodide is readily soluble in water (Schneider, *Pogg.*, 1866, **127**, 624). Stannic sulphate is easily soluble in water, but is decomposed by a large excess (Ditte, *C. r.*, 1887, **104**, 171). Stannous and stannic chloride, and stannic iodide are soluble in alcohol. Stannous nitrate and stannic sulphate, and bromide are *deliquescent*. Stannous sulphide is insoluble in water, soluble in **HCl** with formation of H_2S; decomposed by HNO_3 with oxidation to metastannic acid; insoluble in solution of the normal alkali sulphides, but soluble in the polysulphides with oxidation to a stannic compound (6*c*). Stannic sulphide is soluble in **HCl**, with evolution of H_2S; and in solutions of the alkali sulphides.

6. **Reactions.**—*a.* **Alkali hydroxides** and **carbonates** precipitate from solutions of stannous salts, *stannous hydroxide*, $Sn(OH)_2$ (4), white, readily soluble in excess of the fixed alkali hydroxides, insoluble in water, ammonium hydroxide and the alkali carbonates (distinction from antimony). It is also precipitated by barium carbonate in the cold (Schaffner, *A.*, 1844, **51**, 174).

$$SnCl_2 + 2KOH = Sn(OH)_2 + 2KCl$$
$$Sn(OH)_2 + 2KOH = K_2SnO_2 + 2H_2O$$
$$SnCl_2 + 4KOH = K_2SnO_2 + 2KCl + 2H_2O$$
$$SnCl_2 + Na_2CO_3 + H_2O = Sn(OH)_2 + 2NaCl + CO_2$$

By gently heating the solution of potassium stannite, K_2SnO_2, crystalline stannous oxide, **SnO**, is formed. By rapid boiling of a strong potassium hydroxide solution of stannous hydroxide part of the tin is oxidized and the remainder precipitated as metallic tin: $2K_2SnO_2 + H_2O = Sn + K_2SnO_3 + 2KOH$. The reaction proceeds more rapidly upon the addition of a little tartaric acid. *Stannic salts* are precipitated by **alkali hydroxides** and **carbonates** as *stannic acid*, H_2SnO_3 soluble in excess of the fixed alkali hydroxides, insoluble in ammonium hydroxide and the alkali carbonates (Ditte, *A. Ch.*, 1897 (6), **30**, 282).

$$SnCl_4 + 4KOH = H_2SnO_3 + 4KCl + H_2O$$
$$H_2SnO_3 + 2KOH = K_2SnO_3 + 2H_2O$$
$$SnCl_4 + 6KOH = K_2SnO_3 + 4KCl + 3H_2O$$
$$SnCl_4 + 2Na_2CO_3 + H_2O = H_2SnO_3 + 4NaCl + 2CO_2$$

* Stannous sulphate is decomposed by an excess of cold water forming $2SnSO_4.4SnO.3H_2O$, and by a small amount of hot water forming $SnSO_4.2SnO$ (Ditte, *A. Ch.*, 1882, (5), **27**, 161).

Metastannic salts are precipitated as metastannic acid soluble in potassium hydroxide not too concentrated, not readily soluble in sodium hydroxide, insoluble in ammonium hydroxide excepting when freshly precipitated in the cold, and the alkali carbonates.

b.—**Oxalic acid** forms a white crystalline precipitate with a nearly neutral solution of stannous chloride, soluble in hydrochloric acid, not readily soluble in ammonium chloride. If a nearly neutral solution of stannous chloride be added drop by drop to a solution of ammonium oxalate, the white precipitate which forms at once dissolves in the excess of the ammonium oxalate. Stannic chloride is not precipitated by oxalic acid or ammonium oxalate (Hausmann and Loewenthal, *A.*, 1854, **89**, 104).

Potassium cyanide precipitates both stannous and stannic salts, white, insoluble in excess of the cyanides. **Potassium ferrocyanide** precipitates from stannous chloride solution *stannous ferrocyanide*, $Sn_2Fe(CN)_6$, white, insoluble in water, soluble in hot concentrated hydrochloric acid. From stannic chloride is precipitated a greenish white gelatinous precipitate, soluble in hot hydrochloric acid, but reprecipitated upon cooling (distinction from antimony) (Wyrouboff, *A. Ch.*, 1876, (5), **8**, 458). **Potassium ferricyanide** precipitates from solutions of stannous chloride, *stannous ferricyanide*, $Sn_3(Fe(CN)_6)_2$, white, readily soluble in hydrochloric acid. On warming, the ferricyanide is reduced to ferrocyanide with oxidation of the tin. No precipitate is formed by the ferricyanide with stannic chloride.

c.—The **nitrates** of tin are not stable. Stannous nitrate is *deliquescent* and soon decomposes on standing exposed to the air. Stannous salts when heated with nitric acid are precipitated as SnO_2; but if stannous chloride be warmed with a mixture of equal parts of nitric and hydrochloric acids, stannic chloride and ammonium chloride are formed (Kestner, *A. Ch.*, 1860, (3), **58**, 471).

d.—**Hypophosphorous acid** does not form a precipitate with stannous or stannic chlorides, nor are these salts reduced when boiled with the acid. Sodium **hypophosphite** forms a white precipitate with stannous chloride, soluble in excess of hydrochloric acid; no precipitate is formed with stannic chloride. **Phosphoric acid** and soluble **phosphates** precipitate from solutions of stannous salts, not too strongly acid, *stannous phosphate*, white, of variable composition, soluble in some acids and **KOH**; insoluble in water (Lenssen, *A.*, 1860, **114**, 113). With stannic chloride a white gelatinous precipitate is formed, soluble in **HCl** and **KOH**, insoluble in HNO_3 and $HC_2H_3O_2$. If the stannic chloride be dissolved in excess of **NaOH** before the addition of Na_2HPO_4 and the mixture then acidulated with nitric acid, the tin is completely precipitated as stannic phosphate (separation from antimony). However, the precipitate always carries a little antimony (Bornemann, *Z. angew.*, 1899, 635).

e. **Hydrosulphuric acid** and soluble **sulphides** precipitate from solutions of stannous salts dark brown hydrated *stannous sulphide*, **SnS** (*a*), insoluble in dilute, soluble in moderately concentrated **HCl** (*b*). It is readily dissolved with oxidation by alkali supersulphides, *the yellow sulphides*, forming thiostannates (*c*); from which acids precipitate the yellow stannic sulphide (*d*). The normal, colorless alkali sulphides scarcely dissolve any stannous sulphide at ordinary temperature, compare (§**69**, 6*e* and §**70**, 6*e*), but hot concentrated K_2S dissolves **SnS** forming K_2SnS_3 and **Sn** (*e*) (Ditte, *C. r.*, 1882, **94**, 1419; Baubigny, *J. C.*, 1883, **44**, 22). Potassium and sodium hydroxides dissolve it as stannites and thiostannites (*f*), from which acids precipitate again the brown stannous sulphide (*g*). Ammonium hydroxide and the alkali carbonates do not dissolve it (distinction from arsenic, §**69**, 6*e*). The insolubility in fixed alkali carbonates is a

distinction from antimony (§70, 6e). Nitrohydrochloric acid (free chlorine) dissolves it as stannic chloride, with residual sulphur (h). Nitric acid oxidizes it to metastannic acid without solution (i) (separation from arsenic, §69, 6e).

(a) $SnCl_2 + H_2S = SnS + 2HCl$
(b) $SnS + 2HCl = SnCl_2 + H_2S$
(c) $SnS + (NH_4)_2S_2 = (NH_4)_2SnS_3$
(d) $(NH_4)_2SnS_3 + 2HCl = SnS_2 + 2NH_4Cl + H_2S$
(e) $2SnS + K_2S = K_2SnS_3 + Sn$
(f) $2SnS + 4KOH = K_2SnO_2 + K_2SnS_2 + 2H_2O$
(g) $(K_2SnO_2 + K_2SnS_2) + 4HCl = 2SnS + 4KCl + 2H_2O$
(h) $2SnS + 4Cl_2 = 2SnCl_4 + S_2$
(i) $30SnS + 40HNO_3 + 10H_2O = 6H_{10}Sn_5O_{15} + 40NO + 15S_2$

Solutions of stannic salts are precipitated as *stannic sulphide*, SnS_2, hydrated, yellow, having much the same solubilities as those given for stannous sulphide, with this difference, that stannic sulphide is moderately soluble in normal, colorless, alkali sulphides. The following equations illustrate the most important reactions:

$SnCl_4 + 2H_2S = SnS_2 + 4HCl$
$SnS_2 + 4HCl = SnCl_4 + 2H_2S$
$SnS_2 + (NH_4)_2S = (NH_4)_2SnS_3$
$2SnS_2 + 2(NH_4)_2S_2 = 2(NH_4)_2SnS_3 + S_2$
$3SnS_2 + 6KOH = K_2SnO_3 + 2K_2SnS_3 + 3H_2O$
$(K_2SnO_3 + 2K_2SnS_3) + 6HCl = 3SnS_2 + 6KCl + 3H_2O$
$SnS_2 + 2Cl_2 = SnCl_4 + S_2$
$15SnS_2 + 20HNO_3 + 5H_2O = 3H_{10}Sn_5O_{15} + 15S_2 + 20NO$

Sodium thiosulphate does not form a precipitate with the chlorides of tin (separation from **As** and **Sb**) (Lesser, *Z.*, 1888, **27**, 218). **Sulphurous acid** and sodium **sulphite** precipitate from stannous chloride solution not too strongly acid, *stannous sulphite*, $SnSO_3$, white, readily soluble in **HCl**. When warmed in the presence of hydrochloric acid, sulphur dioxide acts as an oxidizing agent upon the stannous salt. A precipitate of $Sn_6O_{10}S_2$ or SnS_2 is formed, or H_2S is evolved and $SnCl_4$ formed, depending upon the amount of **HCl** present.

$6SnCl_2 + 2SO_2 + 6H_2O = Sn_6O_{10}S_2 + 12HCl$
$6SnCl_2 + 2SO_2 + 8HCl = SnS_2 + 5SnCl_4 + 4H_2O$
$3SnCl_2 + SO_2 + 6HCl = 3SnCl_4 + H_2S + 2H_2O$

Stannic chloride does not give a precipitate with sulphurous acid or sodium sulphite.

The **sulphates** of tin are formed by dissolving the freshly precipitated hydroxides in sulphuric acid and evaporating at a gentle heat. They cannot be formed by precipitation and are decomposed by water (Ditte, *A. Ch.*, 1882, (5), **27**, 145).

f.—**Potassium iodide** added to a concentrated water solution of stannous chloride forms first a yellow precipitate soluble in excess of the $SnCl_2$. Further addition of **KI** gives a yellow precipitate rapidly turning to dark orange needle-like crystals, often forming in rosette-like clusters. If a drop of the stannous chloride solution be added to an excess of potassium iodide the yellow precipitate is formed, which remains permanent unless a further quantity of stannous chloride be added when the orange precipitate is formed. The orange precipitate is probably SnI_2, and is soluble in **HCl**, **KOH**, and C_2H_5OH, soluble in large excess of **KI** and sparingly soluble in H_2O with some decomposition.

The yellow precipitate is probably a double salt of stannous iodide and potassium iodide, and has about the same solubilities as the orange precipitate (Personne, *J.*, 1862, 171; Boullay, *A. Ch.*, 1827, (2), **34**, 372). Potassium iodide in concentrated solution precipitates *stannic iodide*, yellow, from very concentrated water solutions of stannic chloride. The precipitate is readily soluble in water to a colorless solution (Schneider, *J.*, 1866, 229). Hydriodic acid does not give free **I** with Sn^{IV}, distinction from Sb^{V} and As^{V} (Harroun, *J. C.*, 1882, **42**, 661).

The chlorates, bromates and iodates of tin have not been thoroughly studied (*Watts*, **1**, 539, III., 22; *D.*, **2**, 1, 675). Stannous chlorate appears to be formed when potassium chlorate is added to a concentrated water solution of stannous chloride; it dissolves on addition of **HCl**, and nearly all dissolves in excess of water. With $KBrO_3$, bromine is liberated, and with KIO_3 iodine is liberated. Potassium chlorate, bromate and iodate all form precipitates with stannic chloride, soluble in **HCl** without liberation of the halogen.

g.—**Stannous arsenate**, $2SnO.As_2O_5$, a voluminous flocculent precipitate is formed by adding a solution of $SnCl_2$ to a concentrated acetic acid solution of K_3AsO_4, decomposed by heating to **As**, As_2O_3 and SnO_2 (Lenssen, *A.*, 1860, **114**, 115). **Stannic arsenate**, $2SnO_2.As_2O_5$, a white gelatinous precipitate is formed by adding HNO_3 to a mixture of Na_2SnO_3 and Na_3AsO_4 (Haeffely, *J.*, 1855, 395). With antimony, tin acts as a base, forming stannous and stannic antimonites and antimonates (Lenssen, *l. c.*).

h.—If **potassium chromate** be dropped into a hydrochloric acid solution of stannous chloride there is immediate reduction of chromium with formation of a dirty brown precipitate. If stannous chloride be carefully added to potassium chromate in excess, an abundant yellowish precipitate is obtained without much apparent reduction of the chromium. Potassium chromate added to stannic chloride gives an abundance of bright yellow precipitate soluble in excess of $SnCl_4$, insoluble in H_2O, soluble with difficulty in **HCl**. $K_2Cr_2O_7$ also gives a precipitate with $SnCl_2$ and $SnCl_4$ (Leykauf, *J. pr.*, 1840, **19**, 127).

i. An *ammoniacal solution of silver nitrate* is reduced to metallic silver by a solution of *potassium stannite*. The reagent (silver nitrate solution one part, to ammonium hydroxide sixteen parts) serves as a delicate test for the presence of **Sn″** in solution in **KOH**. The addition of **KOH** in excess to an unknown solution removes all heavy metals except **Pb**, **Sb**, **Sn**, **Al**, **Cr**, and **Zn**; of these *tin only* precipitates metallic silver from the strongly ammoniacal solution in the cold. Antimonous and arsenous compounds give the black precipitate of metallic silver if the solution be boiled.

j. A solution of mercuric chloride, $HgCl_2$, reacts with stannous chloride solution, forming $SnCl_4$ and a precipitate of **HgCl** (white) or **Hg°**, gray, depending upon the relative amounts present (§**58**, 6*g*).

k. Stannous salts react with $(NH_4)_2MoO_4$, giving a blue-colored solution of the lower oxides of molybdenum, constituting a delicate test for **Sn″** (§**75**, 6*g*).

7. **Ignition.**—Before the **blow-pipe**, on **charcoal**, with sodium carbonate, and more readily by addition of potassium cyanide, tin is reduced to malleable lustrous globules—brought to view (if minute, under a magnifier) by repeated trituration of the mass with water, and decantation of the lighter particles. A little of the white incrustation of stannic oxide will collect on the charcoal near the mass, and, by persistence of the flame on the globules, the same coating forms upon them. This coating, or oxide of tin, moistened with solution of **cobalt nitrate**, and again ignited strongly, becomes of a blue-green color. SnO_2 fused with **KCN** gives metallic tin (Bloxam, *J. C.*, 1865, **18**, 97).

8. **Detection.**—Tin is precipitated, from the solution acidulated with hydrochloric acid, in the second group by hydrosulphuric acid, as the sulphide (6*e*). By its solution in yellow ammonium sulphide it is separated from the Copper Group (**Hg**, **Pb**, **Bi**, **Cu**, and **Cd**). By the reaction in the Marsh apparatus the tin is reduced to the metal and is not dissolved as long as zinc is still present. The residue **Sn** (**Zn**, **Sb**, **Au**, and **Pt**) in the Marsh apparatus is warmed with hydrochloric acid, which dissolves the **Sn** as $SnCl_2$. This is detected by its reducing action on $HgCl_2$, giving a white precipitate of **HgCl** or a gray one of **Hg**° (6*j*).

A short test for the detection of tin in the stannous condition, or after its reduction to that condition, consists in treating the solution with an excess of cold **KOH** (separation of **Pb**, **Sn**, **Sb**, **Al**, **Cr**, and **Zn**, from all other heavy metals); and adding to this solution, filtered if necessary, a solution of $AgNO_3$ in a great excess of NH_4OH (one part $AgNO_3$ to sixteen parts NH_4OH). A brown-black precipitate of metallic silver indicates that tin was present in the stannous condition (6*i*). Consult also §90 and §92.

9. **Estimation.**—(*1*) Gravimetrically. It is converted into SnO_2, and after ignition weighed. (*2*) Volumetrically. To $SnCl_2$ add $KNaC_4H_4O_6$ and $NaHCO_3$, then some starch solution and a graduated solution of iodine, until a permanent blue coloration appears. (*3*) To $SnCl_2$ add slight excess of $FeCl_3$, and determine the amount of $FeCl_2$ formed, by a graduated solution of $KMnO_4$. (*4*) By electrolytic deposition from a solution of the double oxalate, rendered slightly acid with oxalic acid.

10. **Oxidation.**—Metallic tin reduces solutions of **Ag**, **Hg**, **Bi**, **Cu**, **Pt**, and **Au**, to the metallic state. Sn'' is oxidized to Sn^{IV} by free HNO_2, HNO_3[1], $H_3Fe(CN)_6$, H_2SO_3 and H_2SO_4 (if hot), **Cl**, **HClO**, $HClO_2$, $HClO_3$, **Br**, $HBrO_3$, **I**[3], and HIO_3. Also by **Pb**″ (in alkaline solution only), Pb^{IV}, Ag'[2], Hg', Hg'', As^V, As''' (in presence of **HCl**), Sb^V, Mo^{VI}, Bi''', Cu', $Pd(NO_3)_2$, Pt^{IV}[4], Fe''', Fe^{VI}, Cr^{VI}, Co''', Ni''', and Mn^{2+n}. Chlorine, bromine and iodine act more vigorously in alkaline than in acid mixtures. The above mentioned metallic forms oxidize Sn'' in both acid and alkaline mixtures.

Stannous chloride is one of the most convenient and efficient of the ordinary discriminative deoxidizing agents for operations in the wet way. As stannic chloride is soluble in the solvents of stannous chloride no precipitate of tin is made by its reducing action; but many other metals are so precipitated by reduction to insoluble forms, and are thus identified in analysis, *e. g.*, mercuric chloride is reduced from solution, first to white mercurous chloride, and then to gray mercury (detection of mercury); silver nitrate, to brown-black silver (detection of tin); all soluble com-

[1] Kestner, *A. Ch.*, 1860, (3), **58**, 471. [2] Ditte, *A. Ch.*, 1882, (5), **27**, 145. [3] Thomas, *C. r.*, 1896, **122**, 1539. [4] Ditte, *C. r.*, 1882, **94**, 1114.

pounds of arsenic in strong **HCl** (detection of arsenic); bismuth salts, to metallic bismuth (in alkaline mixture §**76,** 6*g*); and ferric salts, to ferrous salts, left in solution, much used in volumetric analysis of iron (9, and §**126,** 6*g* and 9); auric chloride is reduced to the metal by stannous chloride, forming a colored precipitate varying from brown to reddish-brown or purple-red according to the amount of stannic chloride present. This finely divided precipitate of gold is called "Purple of Cassius" (Max Muller, *J. pr.*, 1884, **30,** 252).

Solutions of Sn^{IV} and Sn'' are reduced to the metallic state by **Cd**, **Al**, **Zn**, and **Mg**. According to Rideal (*C. N.*, 1885, **51,** 292) 0.00003 grams of tin in solution may be detected as the metal by reduction, using the gold zinc wire couple. Stannic salts are reduced to stannous salts by metallic tin, copper or iron (Allen, *J. C.*, 1872, **25,** 274).

§72. Comparison of Certain Reactions of Arsenic, Antimony, and Tin.

Taken as Arsenous Oxide, Arsenic Acid, Antimonous Chloride, Stannous Chloride, Stannic Chloride, or other Soluble Compounds.

	As'''	As^{V}	Sb'''	Sn''	Sn^{IV}
H_2S forms colored sulphides, soluble in $(NH_4)_2S_x$, and in alkalis, reprecipitated by acids.	As_2S_3, lemon yellow, insoluble in HCl, soluble in $(NH_4)_2CO_3$ (§69, 6*e*).	As_2S_5 and As_2S_3, insoluble in HCl, soluble in $(NH_4)_2CO_3$ (§69, 6*e*).	Sb_2S_3, orange, soluble in HCl, insoluble in $(NH_4)_2CO_3$ (§70, 6*e*).	SnS, brownish black, soluble in HCl, insoluble in $(NH_4)_2CO_3$ and in normal sulphides (§71, 6*e*).	SnS_2, yellow, soluble in HCl, insoluble in $(NH_4)_2CO_3$ soluble in normal sulphides (§71, 6*e*).
KOH or NaOH, in excess	No precipitate.	No precipitate.	Sb_2O_3, white, soluble in excess as $KSbO_2$ (§70, 6*a*).	$Sn(OH)_2$, white, soluble in excess as K_2SnO_2 (§71, 6*a*).	H_2SnO_3, white, soluble in excess as K_2SnO_3 (§71, 6*a*).
NH_4OH, in excess.	.....	.....	Sb_2O_3, white, insoluble in excess (§70, 6*a*).	$Sn(OH)_2$, white, insoluble in excess (§71, 6*a*).	H_2SnO_3, white, insoluble in excess (§71, 6*a*).
Zn and dilute H_2SO_4	AsH_3, gas, with $AgNO_3$, gives Ag and H_3AsO_3 (§69, 6′*a* and *b*).	Same as As'''.	SbH_3, gas (also Sb), with $AgNO_3$ forms $SbAg_3$, black (§70, 6*j*; §87; §89, 2).	Sn, grayish black precipitate on the Zn (§90; §92, 5).	Sn″ and then Sn, grayish black (§71, 10).
Dilution of concentrated, nearly neutral, solutions	.....	.....	SbOCl, white, dissolved by tartrates (§70, 5*d*).	Sn_2OCl_2, white, not dissolved by tartrates (§71, 5*c*).	H_2SnO_3. .....
HNO_3, concentrated, acting on the solids	H_3AsO_4, which gives many reactions similar to the phosphates (§69, 6*m*).	Same as with As'''.	Sb_2O_5, insoluble (§70, 4 and 5*b*).	$H_{10}Sn_5O_{15}$, white, insoluble (§71, 4 and 5*b*).	Same as Sn″.
HI	No reaction.	Reduction to As''' with liberation of iodine (§69, 6*f*; §88, 4*d*).	Precipitation of SbI_3, yellow (§70, 6*f*) (with Sb^{V}, iodine is liberated and the Sb^{V} becomes Sb''') (§89, 7).	Precipitation of SnI_2, yellow to orange (§71, 6*f*).	Precipitation of SnI_4, yellow, no reduction (§71, 6*f*).

§73. Gold (Aurum) Au = 197.2. Valence one and three.

1. **Properties.**—*Specific gravity*, 19.30 to 19.34 (Rose, *Pogg.*, 1848, **75**, 403). *Melting point*, 1063° (*Cr. B. S.*, **35**, 1915). It is a yellow metal, that from different parts of the world varying slightly in color; the presence of very small traces of other metals also affects the color. It is softer than silver and harder than tin; possesses but little elasticity or metallic ring. It is the most malleable and ductile of all metals; one gram can be drawn into a wire 2000 metres long. The presence of other metals diminishes the ductility. It may be rolled into sheets 0.0001 mm. thick. At a very high heat it vaporizes (Deville and Debray, *A. Ch*, 1859, (3), **56**, 429). It is a good conductor of electricity, equal to copper, not so good as silver. It has a high coefficient of expansion and cannot be moulded into forms but must be stamped. On account of its softness, gold is seldom used absolutely pure, but is hardened by being alloyed with other metals, as **Ag**, **Cu**, etc.

2. **Occurrence.**—Gold is usually found native, but never perfectly pure, being always alloyed with silver, and occasionally also with other metals. It is found as gold-dust in alluvial sand, sometimes in nuggets, and sometimes disseminated in veins of quartz.

3. **Preparation.**—(**1**) Washing. This consists in treating the well-powdered ore with a stream of water, the heavy gold settling to the bottom. (**2**) Amalgamation. This consists in dissolving the gold in mercury and then separating it from the latter by distillation. (*3*) By fusing with metallic lead, which dissolves the gold, the liquid alloy settling to the bottom of the slag. The gold is afterward separated from the lead by cupellation. The silver is separated from the gold by dissolving it in nitric or sulphuric acid. Or the whole is dissolved in nitrohydrochloric acid, and the gold precipitated in the metallic state by some reducing agent; ferrous sulphate being usually employed. Another method is to pass chlorine into the melted alloy. The silver chloride rises to the surface, while the chlorides of **Zn**, **Bi**, **Sb**, and **As** (if present) are volatilized, and the pure gold remains beneath. A layer of fused borax upon the surface prevents the silver chloride from volatilizing. (*4*) By treatment with a solution of **KCN**. (*5*) By amalgamation with mercury and electrolysis at the same time.

4. **Oxides** and **Hydroxides.**—*Aurous oxide*, Au_2O, is very unstable, heating to about 250°, decomposing it into the metal and oxygen. The hydroxide is prepared by reducing the double bromide with SO_2 in ice-cold solution; heating to 200°, changing it to the oxide (Krüss, *A.*, 1886, **237**, 274). *Auric hydroxide*, $Au(OH)_3$, is prepared by precipitation from the chloride solution with **MgO** (Krüss, *l. c.*). It is a yellow to brown powder, changing to the oxide upon drying at 100°. Heating to 250° gives the metal and oxygen (§**10**).

5. **Solubilities.**—*a.*—*Metal.*—Gold is not at all tarnished or in any way acted upon by water at any temperature, or by hydrosulphuric acid. Neither nitric nor hydrochloric acid attacks it under any conditions; but it is rapidly attacked by **chlorine** (as gas or in water solution), dissolving promptly in nitrohydrochloric acid, as *auric chloride*, $AuCl_3$; by **bromine**, dissolving in bromine water, as *auric bromide*, $AuBr_3$; and by **iodine**; dissolving when finely divided in hydriodic acid by aid of the air and potassium iodide, as *potassium auric iodide*, $KIAuI_3$: $4Au + 12HI + 4KI + 3O_2 = 4KIAuI_3 + 6H_2O$. Potassium cyanide solution, with aid of the air, dissolves precipitated gold as potassium *aurocyanide*, $KAu(CN)_2$: $4Au + 8KCN + O_2 + 2H_2O = 4KAu(CN)_2 + 4KOH$.

Gold is separated, from its alloys with silver and base metals, by solution in **nitric acid**; the gold being left as a black-brown powder—together with platinum and oxides of antimony and tin. When the gold-silver or gold-copper has not over 20 per cent gold, nitric acid of 20 per cent disintegrates the alloy, and effects the separation; when the gold is over 25 per cent, silver or lead (three parts) must be added, by fusion, to the alloy before solution. (If gold-silver alloy contains 60 per cent or more of silver, it is silver color; if 30 per cent silver, a light brass color; if 2 per cent silver, it is brass color.)

If gold and other metals are obtained in solution by **nitrohydrochloric acid**, leaving most of the silver as a residue, the noble metals can be precipitated by **zinc** or ferrous sulphate, and the *precipitate* of gold, silver, etc., treated with

nitric acid, which will now dissolve out any proportion of silver not less than 15 per cent, to 85 per cent of gold, and dissolve the baser metals. Concentrated sulphuric acid dissolves silver, and leaves gold.

b.—The *oxides* and *hydroxides* of gold are insoluble in water, soluble in acids. *c.*—The *salts* of the oxyacids are not stable, being decomposed by hot water. Gold sulphide is insoluble in water or acids, except nitrohydrochloric acid, soluble in alkali sulphides. Aurous salts are decomposed by water, forming Au° and Au'''. Auric chloride is *deliquescent*; both the chloride and bromide are readily soluble in water. The iodide is decomposed by water, forming aurous iodide. The double chlorides, bromides, iodides and cyanides are soluble in water.

6. **Reactions.** *a.* The **fixed alkali hydroxides** and **carbonates** in excess do not precipitate $AuCl_3$ solutions, as a soluble aurate, $KAuO_2$, readily forms; but upon boiling and neutralizing the excess of alkali, $Au(OH)_3$ is precipitated. **Ammonium hydroxide** precipitates from concentrated solutions a reddish-yellow ammonium aurate, $(NH_3)_2Au_2O_3$, "fulminating gold." *b.* **Oxalic acid** reduces gold chloride from solutions, slowly (nitric acid should be absent and the presence of ammonium oxalate is advantageous), but completely. The gold separates in metallic flakes or forms a mirror on the side of the test-tube. $2AuCl_3 + 3H_2C_2O_4 = 2Au + 6CO_2 + 6HCl$. As platinum, palladium, and other second group metals are not reduced by oxalic acid, this method of removal of gold should be employed upon the original solution before the precipitation of the **second group** metals as sulphides. Potassium gold cyanide, $KCN.Au(CN)_3$, is formed when a neutral solution of $AuCl_3$ is added to a hot saturated solution of **KCN**. It is very soluble in water and by heating above 200° it is decomposed into **CN** and $KCN.AuCN$, which latter product is formed when gold is dissolved in **KCN** in the presence of air (*5a*). *c.* A solution of $AuCl_3$ is precipitated as Au° by a solution of KNO_2. *d.* **Sodium pyrophosphate** forms with $AuCl_3$ a double salt which has found application in gold plating. *e.* **Hydrosulphuric acid** precipitates from gold chloride solution, hot or cold, *gold sulphide*, variable from Au_2S to Au_2S_3, brown, insoluble in acids, hot or cold, except in nitrohydrochloric acid, in which it readily dissolves; soluble in alkali sulphides to a thio-salt. **Alkali sulphites** precipitate gold chloride solution as *double sulphite*, *i. e.* $Au_2(SO_3)_3.(NH_4)_2SO_3.6NH_3 + 3H_2O$. Upon boiling the sulphite acts as a reducing agent, giving metallic gold.

f. **Potassium iodide,** added in small portions *to* solution of auric chloride (so that the latter is constantly in excess where the two salts are in contact), and when equivalent proportions have been reached, gives a yellow precipitate of *aurous iodide*, AuI, insoluble in water, soluble in large excess of the reagent; the precipitate accompanied with separation of free iodine, brown, which is quickly soluble in small excess of the reagent as a colored solution: $AuCl_3 + 4KI = AuI + 3KCl + I_2$ with KI. But, on gradually adding auric chloride to solution of potassium iodide, so that the

latter is in excess at the point of chemical change, there is first a dark-green solution of potassio-auric iodide, $KIAuI_3$; then a dark-green precipitate of *auric iodide,* AuI_3 , very unstable, decomposed in pure water, more quickly by boiling; changed in the air to the yellow aurous iodide.

g. **Stannous chloride** gives a purple precipitate containing the oxides of tin with the gold, "**purple of Cassius**" insoluble in acids.

h. **Ferrous sulphate** is the most common reagent for the detection of gold, reducing all gold salts to the metallic state; $AuCl_3 + 3FeSO_4 = Au + Fe_2(SO_4)_3 + FeCl_3$.

7. **Ignition.**—Gold is reduced from many of its compounds by **light,** and from all of them by **heat**—its separation **in the dry way** being readily effected by fusion with such reagents as will make the material fusible. Very small proportions are collected in alloy with lead, by fusion; after which the lead is vaporized in "**cupellation**" (§59, 7).

8. **Detection.**—In the dry way gold is detected by fusion of the mineral matter with lead, to the formation of a "button" which is then ignited to drive off the lead, leaving the gold and silver behind as the metals. In the wet way the material, if not in solution, is digested with nitro-hydrochloric acid which dissolves all the gold. The excess of acid is removed by evaporation and the gold is precipitated by oxalic acid or ferrous sulphate, and identified by its color and insolubility in acids. If the gold be not removed from the original solution it is precipitated in Group II. by H_2S , passes into Division A (tin group) by $(NH_4)_2S$, and may be detected in the flask of the Marsh apparatus by the usual methods.

9. **Estimation.**—Gold is always weighed in the metallic state, to which form it is reduced: (*1*) By ignition alone if it is a salt containing no fixed acid; if in an ore, by mixing with lead and fusion to an alloy, and final removal of the lead by ignition at a white heat in presence of air. (*2*) By adding to the solution some reducing agent, usually $FeSO_4$, $H_2C_2O_4$, chloral hydrate, or some easily oxidized metal, such as **Zn** , **Cd** , or **Mg** . (*3*) Gold is also estimated volumetrically by $H_2C_2O_4$ and the excess of $H_2C_2O_4$ used, determined by $KMnO_4$.

10. **Oxidation.**—Gold is reduced to the metallic state by very many reducing agents, among which may be mentioned the following: **Pb** , **Ag** , **Hg** , **Hg′**, **Sn** , **Sn″**, **As** , **As‴**, AsH_3 , **Sb** , **Sb‴**, SbH_3 , **Bi** , **Cu** , **Cu′**, **Pd** , **Pt** , **Te** , **Fe** , **Fe″**, **Al** , **Co** , **Ni** , **Cr‴**, **Zn** , **Mg** , $H_2C_2O_4$, HNO_2 , **P** , H_3PO_2 , H_3PO_3 , PH_3 , H_2SO_3 , and a great number of organic substances.

§74. Platinum. Pt. = 195.2 . Valence two and four.

1. **Properties.**—*Specific gravity* at 17.6°, 21.48 (Deville and Debray, *C. r.* 1860, **50**, 1038). *Melting point,* 1755° (*Cr. B. S.*, **35**, 1915). Pure platinum is a tin-white metal, softer than silver, hardened by the presence of other metals, especially iridium, which it frequently contains. It is surpassed in ductility and malleability only by **Au** and **Ag.** *Platinum black* is the finely divided metal, a black powder, obtained by reducing an alkaline solution of the platinous salt with alcohol (Low, *B.*, 1890, **23**, 289); *platinum sponge,* a gray spongy mass, by ignition of the platinum ammonium double chloride; *platinized asbestos* (usually 10 per cent **Pt**), the metal in finely divided form deposited by reduction

from the salt upon asbestos. These finely divided forms of platinum have great power of condensation of gases, and by their presence alone bring about a number of important chemical reactions (catalytic reaction); *e. g.*, a current of hydrogen mixed with air ignites when passed over platinum black, also hydrogen and chlorine unite. SO_2 unites with O to form SO_3; alcohol is oxidized to acetic acid, formic and oxalic acids to CO_2, AS''' to As^v, etc.

2. **Occurrence.**—Found in nature in the metallic state, generally alloyed with palladium, iridium, osmium, rhodium, ruthenium, etc. The Ural Mountains furnish the largest supply of platinum. The only known native compound is sperrylite, $PtAs_2$, found in Ontario, Canada, and Macon Co., N. Car.

3. **Preparation.**—Usually by the wet method. The finely divided ore is treated with nitrohydrochloric acid until the platinum is all dissolved. The filtrate is then treated with lime water to a slightly acid reaction; this removes the greater part of the Fe, Cu, Ir, Rh, and a portion of the Pd. The filtrate is now evaporated to dryness, ignited and washed with water and hydrochloric acid. This gives a commercial platinum which is melted with six times its weight of lead and the finely divided alloy digested with dilute HNO_3, which dissolves out the Pb, Cu, Pd, and Rh. The black powder which remains is dissolved in nitrohydrochloric acid, the Pb remaining, removed with H_2SO_4, and the Pt precipitated with NH_4Cl. The precipitate contains a little rhodium, which is removed by gently igniting the mass with potassium and ammonium di-sulphate, and exhausting with water, which dissolves out the rhodium sulphate (§105, 7). In the laboratory the platinum residues are boiled with KOH or K_2CO_3 and reduced with alcohol. The fine black powder is filtered, washed with water and hydrochloric acid and ignited.

4. **Oxides and Hydroxides.**—Platinum forms two oxides, PtO and PtO_2. *Platinous hydroxide* is formed by treating a dilute solution of platinous potassium chloride with NaOH and boiling (Jörgensen, *J. pr.*, 1877, (2), **16**, 344). A black powder easily soluble in HCl or HBr, reduced by formic acid to Pt°, gentle heating changes it to the oxide PtO. *Platinic hydroxide*, $Pt(OH)_4$, is formed by treating a solution of H_2PtCl_6 with Na_2CO_3 in excess, evaporating to dryness, washing with water and then with acetic acid. It is a red-brown powder, soluble in NaOH, HCl, HNO_3, and H_2SO_4; insoluble in $HC_2H_3O_2$. Gentle heating changes it to the oxide PtO_2 (Topsoe, *B.*, 1870, **3**, 462).

5. **Solubilities.**—*a.—Metal.*—Platinum is not affected by air or water, at any temperature; is not sensibly tarnished by hydrosulphuric acid gas or solution; and is not attacked at any temperature by nitric acid, hydrochloric acid or sulphuric acid, but dissolves in nitrohydrochloric acid less readily than gold. The substance obtained by evaporating an aqua regia solution of platinum is platinic chloride plus 2 molecules of hydrochloric acid, $PtCl_4.2HCl$. This salt is frequently called platinic chloride and its water solution is the platinic chloride reagent. It is more correctly called *chlorplatinic acid* and the formula written H_2PtCl_6. *b.—Oxides* and *hydroxides.*—See 4. *c.—Salts.*—Platinum forms two classes of salts (both haloid and oxy), platinous and platinic. The oxysalts are not stable. None of the platinous salts are permanently soluble in pure water. The chloride is soluble in dilute hydrochloric acid and the sulphate in dilute sulphuric acid. **Platinic** *chloride*, $PtCl_4$, and bromide, all the platinicyanides (as $PbPt(CN)_6$), and the platinocyanides of the metals of the alkalis and alkaline earths (as $K_2Pt(CN)_4$), are **soluble** in water. The platinous and platinic nitrates are soluble in water, but easily decomposed by it, with the precipitation of basic salts. The larger number of the *metallo-platinic chlorides* or "chloroplatinates" are soluble in water, including those with sodium [Na_2PtCl_6 or $(NaCl)_2PtCl_4$], barium, strontium, magnesium, zinc, aluminum, copper; and those with potassium, and ammonium, are sparingly soluble in water, and owe their analytical importance as complete precipitates to their insolubility in alcohol. Of the *metallo-platinous chlorides* (the "chloroplatinites")—those with sodium [Na_2PtCl_4], and barium, are soluble; zinc, potassium and ammonium, sparingly soluble; lead and silver, insoluble in water. Platinic *sulphate*, $Pt(SO_4)_2$, is soluble in water (§10).

6. **Reactions.**—*a.*—*Platinous chloride*, $PtCl_2$, is precipitated by KOH as $Pt(OH)_2$, soluble in excess of the reagent to K_2PtO_2, *potassium platinite*, which solution is reduced by alcohol to "platinum black" (1). *Platinic chloride*, H_2PtCl_6, a brown-red solid, soluble in alcohol and water, forms with KOH or NH_4OH, not too dilute, a yellow crystalline precipitate of an alkali (K or NH_4),

chlorplatinate, *e. g.*, K_2PtCl_6, sparingly soluble in water, soluble in excess of the alkalis and reprecipitated by hydrochloric acid. K_2CO_3 and $(NH_4)_2CO_3$ give the same precipitate, insoluble in excess of the reagent. A more complete precipitation of the **K** or NH_4 is obtained by the use of the chlorides. The sodium platinum chloride, Na_2PtCl_6, is very soluble in water and is not formed by precipitation with sodium salts. *b.*—**Oxalic acid** does not reduce platinum salts (distinction from gold). A solution of chloral hydrate precipitates platinum from its solutions. Platinous and platinic salts form with **cyanides** a great number of double salts. *c.*—See 5*c*. *d.*—**Hypophosphorous acid** reduces platinum salts to metallic platinum. **Phosphates** do not precipitate platinum salts.

e. **Hydrosulphuric** acid precipitates solutions of the *platinous* salts as the black sulphide, **PtS**, insoluble in acids, sparingly soluble in water and in alkali sulphides; *platinic* salts are precipitated as platinic sulphide, PtS_2, black; slowly soluble in alkali sulphides (Ribau, *C. r.*, 1877, **85**, 283), insoluble in acids except nitrohydrochloric. **Sulphur dioxide** decolors a solution of platinum chloride giving a compound which does not respond to the usual reagents for platinum and requires long boiling with **HCl** for the removal of the SO_2 (Birnbaum, *A.*, 1871, **159**, 116).

f. The **chlorides** of potassium and ammonium are estimated quantitatively by precipitation from their concentrated solutions with a solution of platinic chloride. **Potassium iodide** colors a solution of platinum chloride brown-red and precipitates the black platinic iodide, PtI_4, excess of the **KI** forming K_2PtI_6, brown, sparingly soluble (5*c*). *g.* **Stannous chloride** does not precipitate the platinum from platinic chloride (distinction from gold), but reduces it to platinous chloride.

h. **Ferrous sulphate** solution on boiling with a platinum chloride solution precipitates the platinum as the metal, the presence of acids hinders the reduction.

7. **Ignition.**—All platinum compounds upon ignition are reduced to the metal. Owing to the high point of fusibility of the metal and to the difficulty with which it is attacked by most chemicals, platinum has an extended use in the **chemical laboratory** for evaporating dishes, crucibles, foil, wire, etc. IN THE USE OF PLATINUM APPARATUS WITHOUT UNNECESSARY INJURY IT SHOULD BE REMEMBERED:

(*1*) That free *chlorine* and *bromine* attack platinum at ordinary temperatures (forming platinic chloride, bromide); and free *sulphur*, *phosphorus*, arsenic, *selenium*, and iodine, attack *ignited* platinum (forming platinous sulphide, platinic phosphide, platinum-arsenic alloy, platinic selenide, iodide). Hence, the fusion of sulphides, sulphates, and phosphates, *with reducing agents*, is detrimental or fatal to platinum crucibles. The ignition of organic substances containing phosphates acts as free phosphorus, in a slight degree.

The heating of ferric chloride, and the fusion of bromides, and iodides, act to some extent on platinum.

(2) The *alkali hydroxides* (not their carbonates) and the alkaline earths, especially baryta and lithia, with *ignited* platinum *in the air*, gradually corrode platinum (by formation of platinites: $2Pt + 2BaO + O_2 = 2BaPtO_2$. Silver crucibles are recommended for fusion with alkali hydroxides.

(3) All **metals** *which may be reduced in the fusion—especially compounds of lead, bismuth, tin,* and other metals easily reduced and melted—and all *metallic compounds with reducing agents* (including even alkalis and earths) form fusible alloys with ignited platinum. Mercury, lead, bismuth, tin, antimony, zinc, etc., are liable to be rapidly reduced, and *immediately to melt away platium* in contact with them.

(4) *Silica with charcoal* (by formation of silicide of platinum) corrodes ignited platinum, though very slowly. Therefore, platinum crucibles should not be supported on charcoal in the furnace, but in a bed of magnesia, in an outer crucible of clay. Over the flame, the best support is the triangle of platinum wire.

(5) The tarnish of the gas-flame increases far more rapidly upon the already tarnished surface of platinum—going on to corrosion and cracking. The surface should be kept polished—preferably by gentle rubbing with moist *sea-sand* (the grains of which are perfectly rounded, and *do not scratch* the metal). Platinum surfaces are also **cleansed** by fusing *borax* upon them, and by digestion with nitric acid.

8. **Detection.**—Platinum is identified by the appearance of the reduced metal; by its insolubility in **HCl** or HNO_3 and solubility in $HNO_3 + HCl$; and by its formation of precipitates with ammonium and potassium chlorides and **KI**. It is separated from gold by boiling with oxalic acid and ammonium oxalate, which precipitate the gold, leaving the platinum in solution. The filtrate from the gold should be evaporated, ignited, and the residue examined and after proving insolubility in **HCl** or HNO_3, dissolved in HNO_3 and **HCl** and the presence of platinum confirmed with NH_4Cl. If the gold and platinum have been precipitated in the second group with H_2S and dissolved with $(NH_4)_2S_x$ they may be separated from **As**, **Sb**, and **Sn** by dissolving the reprecipitated sulphides in $HCl + KClO_3$, evaporating to remove the chlorine and boiling after adding **KOH** in excess, with **chloral hydrate**, which precipitates the **Au** and **Pt**, leaving the **As**, **Sb**, and **Sn** in solution. The **Au** and **Pt** may then be dissolved in $HNO_3 + HCl$ and separated as directed above. $FeSO_4$ may be use to precipitate **Au** and **Pt**, separating them from **As**, **Sb**, and **Sn**.

9. **Estimation.**—Platinum is invariably weighed in the metallic state. It is brought to this condition: (1) By simple ignition; (2) by precipitation as $(NH_4)_2PtCl_6$, K_2PtCl_6, or PtS_2 and ignition; (3) by reduction, using **Zn**, **Mg**, or $FeSO_4$.

10. **Oxidation.**—Solutions of platinum are reduced to the metallic state by the

following metals: **Pb**, **Ag**, **Hg**, **Sn** (**Sn″** to **Pt″** only), **Bi**, **Cu**, **Cd**, **Zn**, **Fe**, **Fe″**, **Co**, and **Ni**. Very many organic substances reduce platinum compounds to the metallic state.

§75. Molybdenum. **Mo** = 96.0. Valence two, three, four and six.

1. **Properties.**—*Specific gravity*, 9.01 (Moissan, *C. R.*, **120**, 1895). *Melting point*, 2500°? (*Cr. B. S.*, **35**, 1915). It is a silver-white, hard, brittle metal, not oxidized in the air or water at ordinary temperatures. Upon heating in the air it becomes brown, then blue, and finally burns to the white MoO_3. Heated to a red heat in contact with steam, it forms first a blue oxide, then MoO_3.

2. **Occurrence.** — Not found native, but occurs chiefly as molybdenite, MoS_2; as an oxide in molybdenum ochre, molybdite, MoO_4; and as wulfenite, $PbMoO_4$.

3. **Preparation.**—(*1*) By heating the oxide, sulphide or chloride in a current of oxygen free hydrogen (von der Pfordten, *B.*, 1884, **17**, 732; Rogers and Mitchell, *J. Am. Soc.*, 1900, **22**, 350); (*2*) by heating with **C** and Na_2CO_3; (*3*) by heating MoO_3 with **KCN** (Loughlien, *l. c.*).

4. **Oxides** and **Hydroxides.**—*Molybdous hydroxide*, $MoO.xH_2O$, is formed when molybdous chloride or nitrate is precipitated with alkali hydroxides or carbonates, dark brown becoming blue in the air by oxidation. $Mo(OH)_3$, black, turning red-brown by oxidation in the air, is formed by treating $MoCl_3$ with **KOH**; also by electrolysis of ammonium molybdate (Smith, *B.*, 1880, **13**, 751). By heating the hydroxide in a vacuum Mo_2O_3 is obtained as a black mass, insoluble in acids. MoO_2, a dark bluish mass, insoluble in **KOH** or **HCl**, is formed by igniting a mixture of ammonium molybdate, potassium carbonate and boric acid, and exhausting the fused mass with water (Muthmann, *A.*, 1887, **238**, 114). *Molybdic anhydride* (acid), MoO_3, white, occurs in nature; it is obtained by the ignition of the lower oxidized compounds in the air or in the presence of oxidizing agents.

5. **Solubilities.**—Molybdenum is readily soluble in nitric acid with oxidation to MoO_3, evolving **NO**; in hot concentrated sulphuric acid, evolving SO_2. The various lower oxides of molybdenum are soluble in acids forming corresponding salts, not very stable, oxidizing on exposure, to molybdic acid and molybdates; on the other hand, reducing agents reduce molybdates to the lower forms of molybdenum salts, nearly all of which are colored brown to reddish brown or violet. The salts of molybdenum are nearly all soluble in water. Molybdic anhydride, MoO_3, white, is sparingly soluble in water and possesses basic properties towards stronger acids, dissolving in them to form salts. The chlorides and the sulphates are soluble in water (Schulz-Sellack, *B.*, 1871, **4**, 14); the nitrates in dilute nitric acid. The anhydride MoO_3 combines with the alkalis to form molybdates, soluble in water. Molybdates of the other metals are insoluble in water. Solutions of the alkali molybdates are decomposed by acids forming, MoO_3, which dissolves in excess of the acids.

6. **Reactions.**—*a.*—The dyad, triad and tetrad molybdenum salts are precipitated by the **alkali hydroxides** and **carbonates**, forming the corresponding hydroxides, insoluble in excess of the precipitant. These hydroxides oxidize in the air to a blue molybdenum molybdate. *b.*—A solution of a molybdate acidulated with hydrochloric acid gives no red color with **KCNS** (distinction from **Fe‴**); but if **Zn** be added, reduction to a lower oxide of molybdenum takes place and an intense red color is produced. Phosphoric acid does not destroy the color (difference from ferric thiocyanate). Upon shaking with ether the sulphocyanate is dissolved in the ether, transferring the red color to the ether layer. In molybdic acid solutions, acidulated with hydrochloric acid, **potassium ferrocyanide** gives a reddish brown precipitate. An alkaline solution of molybdates is colored a deep red to brown by a solution of tannic acid. *c.*—See 5.

d—**Tribasic phosphoric** acid and its salts precipitate, from strong nitric acid solutions of ammonium molybdate,* somewhat slowly, more rapidly on warming, *ammonium phospho-molybdate* ($(NH_4)_3PO_4.12MoO_3.3H_2O$), yellow, of variable composition, soluble in ammonium hydroxide and other alkalis, sparingly soluble in excess of the phosphate. The *sodium phospho-molybdate* is soluble in water, and precipitates ammonium from its salts; also, it precipitates the alkaloids—for which reaction it has some importance as a reagent.† Arsenic acid and **arsenates** give the same reaction; *ammonium arseno-molybdate* being formed (*g*).

e.—Neutral or alkaline **solutions of** molybdates are colored yellow to brown by **hydrosulphuric acid** but are not precipitated. From the acid solutions a small amount of the hydrogen sulphide gives no precipitate but colors the solution blue; with more hydrosulphuric acid the brown or red-brown precipitate, MoS_3, *molybdenum trisulphide*, is obtained after some time. The precipitate is soluble in ammonium sulphide, better when hot and not too concentrated, as ammonium thiomolybdate, $(NH_4)_2MoS_4$, from which acids precipitate the trisulphide (Berzelius, *Pogg.*, 1826, **7**, 429), soluble in nitric acid, insoluble in boiling solution of oxalic acid (separation from stannic sulphide).

If $Na_2S_2O_3$ be added to a solution of ammonium molybdate, slightly acid, a blue precipitate and blue-colored solution is obtained. If the solution be more strongly acid, a red brown precipitate is obtained. An acid solution of a molybdate treated with hypophosphorous and **sulphurous** acids gives an intense bluish green precipitate or color, depending upon the amount of molybdenum present.

f.—Halogen compounds not important in analysis of molybdenum.

g.—**Arsenic acid** and **arsenates** form, with a nitric acid solution of ammonium molybdate, a yellow precipitate of *ammonium arseno-molybdate*, in appearance and reactions not to be distinguished from the ammonium phospho-molybdate; except the precipitation does not take place until the solutions are slightly warmed, while with phosphates the precipitation begins even in the cold. Stannous salts give with $(NH_4)_2MoO_4$ a blue solution of the lower oxides of molybdenum (a delicate test for Sn″) (Longstaff, *C. N.*, 1899, **79**, 282).

h.—The alkali molybdates are soluble in water and their solutions precipitate solutions of nearly all other metallic salts, forming molybdates of the corresponding metals, insoluble in water, *e. g.*, $K_2MoO_4 + Pb(NO_3)_2 = PbMoO_4 + 2KNO_3$.

* The reagent ammonium molybdate, $(NH_4)_2MoO_4$, is prepared by dissolving molybdic acid, MoO_3 (100 grams), in ammonium hydroxide (250 cc. sp. gr. 0.90 with 250 cc. water) cooling, and slowly pouring this solution into well cooled fairly concentrated nitric acid (750 cc. sp. gr. 1.42 with 750 cc. water) with constant stirring.

† *Sodium Phospho-molybdate*—Sonnenschein's reagent for acid solutions of alkaloids—is prepared as follows: The yellow precipitate formed on mixing acid solutions of ammonium molybdate and sodium phosphate—the ammonium phospho-molybdate—is well washed, suspended in water, and heated with sodium carbonate until completely dissolved. The solution is evaporated to dryness, and the residue gently ignited till all ammonia is expelled, sodium being substituted for ammonium. If blackening occurs, from reduction of molybdenum, the residue is moistened with nitric acid, and heated again. It is then dissolved with water and nitric acid to strong acidulation; the solution being made ten parts to one part of residue. It must be kept from contact with vapor of ammonia, both during the preparation and when preserved for use.

7. **Ignition.**—With microcosmic salt, in the outer blow-pipe flame, all compounds of molybdenum give a bead which is greenish while hot, and colorless on cooling; in the inner flame, a clear green bead. With borax, in the outer flame, a bead, yellow while hot, and colorless on cooling; in the inner flame, a brown bead, opaque if strongly saturated (molybdous oxide). On charcoal, in the outer flame, molybdic anhydride is vaporized as a white incrustation; in the inner flame (better with sodium carbonate), metallic molybdenum is obtained as a gray powder, separated from the mass by lixiviation. Dry molybdates, heated on platinum foil with concentrated sulphuric acid to vaporization of the latter form, on cooling in the air, a blue mass.

8. **Detection.**—In the ordinary process of analysis, molybdenum appears in Division B (tin group) of the **second group** with **As**, **Sb**, **Sn**, **Au**, and **Pt**. The sulphide is insoluble in strong hydrochloric acid but dissolves together with the **As** and **Pt** in aqua regia or potassium chlorate and hydrochloric acid. On evaporation the platinum is precipitated as potassium chlorplatinate. From the filtrate the arsenic may be precipitated by means of magnesia mixture and the gold by heating with oxalic acid. The molybdenum remains in solution as molybdic acid. This solution, evaporated to dryness, dissolved in ammonium hydroxide and poured into moderately concentrated **HCl** forms a solution of ammonium molybdate which may be identified by the many precipitation and reduction tests (6 *b*, *c*, *d*, *e*, *i*, etc., 7, and 9). If the molybdenum be present as a molybdate it may be precipitated from its nitric acid solution by Na_2HPO_4, washed, dissolved in ammonium hydroxide, the phosphate removed by magnesia mixture (§**189**, 6*a*), and the filtrate evaporated to crystallization (Maschke, *Z.*, 1873, **12**, 380). The crystals may be tested by the various reduction tests for molybdenum.

9. **Estimation.**—(*1*) Molybdic anhydride and ammonium molybdate may be reduced to the dioxide by heating in a current of hydrogen gas. The heat must not be permitted to rise above dull redness. Or the temperature *may* rise to a white heat, which reduces it to the metallic state, in which form it is weighed. (*2*) Lead acetate is added to the alkali molybdate, the precipitate washed in hot water, and after ignition weighed as $PbMoO_4$. (*3*) Volumetrically. The molybdic acid is treated with zinc and **HCl**, which converts it into $MoCl_3$. This is converted into molybdic acid again by standard solution of potassium permanganate.

10. **Oxidation.**—**Reducing agents** convert molybdic acid either into the *blue* intermediate oxides, or, by further deoxidation, into the *black* molybdous oxide, **MoO**. In the (hydrochloric) acid solutions of molybdic acid, the blue or black oxide formed by reduction, will be held in solution with a blue or brown color. Nitric acidulation is, of course, incompatible with the reduction. Certain reducing agents act as follows:

Cane sugar in the feebly acid boiling solution, forms the *blue* color—seen better after dilution; a delicate test. **Stannous chloride** forms first the *blue*, then the *brown*, or the *greenish* brown to black-brown, solution of both the intermediate oxide and the molybdous oxide. **Zinc**, with **HCl** or H_2SO_4, gives the *blue*, then *green*, then *brown* color, by progressive reduction. Formic and oxalic acids do not react. A solution of 1 milligram of sodium (or ammonium) molybdate in 1 cc. of concentrated sulphuric acid (about 1 part to 1840 parts) is in use as Frœhde's Reagent for alkaloids. The molybdenum in this solution, which must be freshly prepared for use each time, is reduced by very many organic substances; and with a large number of alkaloids, it gives distinctive colors, blue, red, brown and yellow.

The Copper Group (Second Group, Division B).

Mercury (Mercuricum), Lead, Bismuth, Copper, Cadmium (Ruthenium, Rhodium, Palladium, Osmium).

§76. Bismuth, Bi = 208.0. Valence three and five.

1. **Properties.**—*Specific gravity*, 9.7474 (Classen, *B.*, 1890, **23**, 938); *melting point*, 271° (*Cir. B. S.*, **35**, 1915); it vaporizes at 1700° and the density of the vapor shows that the molecule **Bi** has begun to dissociate (Biltz and V. Meyer, *B.*, 1889, **22**, 725). It is a hard, brittle, reddish-white, lustrous metal: forming beautiful rhombohedral crystals when a partially cooled mass is broken into and the still molten mass decanted. Alloys of bismuth with other metals give compounds of remarkably low melting points, *e. g.*, an alloy of: **Pb** three, **Sn** four, **Bi** fifteen, and **Cd** three by weight melts at 55.5°; and an alloy of: **Bi** four, **Pb** two, **Sn** one, and **Cd** one parts by weight melts at 65.5° "Wood's Metal." *

2. **Occurrence.**—It is a comparatively rare metal, not very widely distributed; frequently found native. It is found in greatest quantities in Saxony; also found in Bohemia, France, England and South America. As mineralogical varieties it occurs as Bismite (Bi_2O_3), bismutite ($4Bi_2O_3.3CO_2.4H_2O$), bismuthinite (Bi_2S_3), etc.

3. **Preparation.**—The rock containing bismuth, usually with large amounts of cobalt, etc., is roasted to remove sulphur and arsenic, which is nearly always present. The mass is then fused with charcoal. The molten bismuth settles to the bottom below the layer of cobalt. The cobalt becomes solid while the bismuth is still molten, and the two are separated mechanically. The metal is further purified by melting with KNO_3 or **KCN**.

4. **Oxides.**—*Bismuth trioxide*, Bi_2O_3, is formed by heating the metal in the presence of air, or by igniting the hydroxide; it is a pale citron-yellow powder. The hydroxide, $Bi(OH)_3$, white, is formed by precipitating a solution of a salt of bismuth with an alkali hydroxide. If bismuth chloride is used the hydroxide formed always contains some oxychloride, **BiOCl** (Strohmeyer, *Pogg.*, 1832, **26**, 549). The meta hydroxide, **BiO(OH)**, is formed upon drying the orthohydroxide at 100° (Arppe, *Pogg.*, 1845, **64**, 237). *Bismuth pentoxide*, Bi_2O_5, is formed by igniting $Bi(OH)_3$ with excess of **KOH** or **NaOH** in presence of the air, and washing the cooled mass repeatedly with cold dilute nitric acid (Strohmeyer, *l. c.*); or by treating $Bi(OH)_3$ with three per cent H_2O_2 in strong alkaline solution (Hasebrock, *B.*, 1887, **20**, 213). It is a heavy dark brown powder. At 150° it gives off **O**, and at the temperature of boiling mercury becomes Bi_2O_3. It is decomposed in the cold by **HCl** with evolution of chlorine. *Bismuthic acid*, $HBiO_3$, or more probably $Bi_2O_5.H_2O$, is formed upon conducting a rapid current of chlorine into $Bi(OH)_3$ suspended in concentrated **KOH** solution. It is a beautiful scarlet red powder which at 120° gives off its water, becoming Bi_2O_5 (Muir, *J. C.*, 1876, **29**, 144; Muir and Carnegie, *J. C.*, 1887, **51**, 86). It is doubtful if any alkali salt of bismuthic acid exists, although mixtures of $KBiO_3$ and $HBiO_3$ are claimed by Hoffmann (*A.*, 1884, **223**, 110), and André (*C. r.*, 1891, **113**, 860). The so-called *bismuth tetroxide*, Bi_2O_4, is probably a mixture of the trioxide and pentoxide (§12).

5. **Solubilities.**—*a.—Metal.*—Metallic bismuth is insoluble in hydrochloric acid †; soluble in warm concentrated sulphuric acid with evolution of sulphur dioxide; readily soluble in nitric acid and in nitrohydrochloric acid. It burns in chlorine with production of light; it combines with bromine, but more slowly than antimony; it combines readily upon fusing together with **I**, **S**, **Se**, **Te**, **As**, and **Sb**, besides the many metals with which it combines to form com-

* For other fusible alloys see Van Nostrand's Chemical Annual, 3d issue, p. 376.

† A trace of bismuth can always be found in solution when the metal is boiled with hydrochloric acid, but no more than when the metal has been boiled with pure water (Ditte and Metzner, *A. Ch.*, 1896, (6), **29**, 389).

mercial alloys (1). The halogen derivatives of pentad bismuth are not known (Muir, *J. C.*, 1876, **29**, 144). *b—Oxides and hydroxides.*—Bismuth oxide, Bi_2O_3, and the hydroxides, $Bi(OH)_3$ and $BiO(OH)$, are soluble in hydrochloric, nitric and sulphuric acids; insoluble in water and the alkali hydroxides or carbonates. The presence of glycerol prevents the precipitation of bismuth hydroxides from solutions of its salts by the alkalis.* Bismuth pentoxide, Bi_2O_5, is soluble in **HCl**, **HBr**, and **HI** with evolution of the corresponding halogen and formation of the triad salt. Nitric and sulphuric acids in the cold have but little or no action; when hot the triad bismuth salt is formed with evolution of oxygen.

c.—Salts.—Most of the salts of bismuth are insoluble in water. The chloride, bromide, iodide, nitrate, and sulphate are soluble in water acidulated with their respective acid, or with other acids forming "soluble" bismuth salts. Pure water decomposes the most of the solutions of bismuth salts forming corresponding oxy-salts (§**70**, 5*d* footnote).

The chloride, bromide and sulphate are deliquescent.

d.—**Water.**—A solution of bismuth chloride in water acidulated with hydrochloric acid is precipitated on further dilution with water, bismuth oxy-chloride, **BiOCl** being formed; *e. g.*, $BiCl_3 + H_2O = BiOCl + 2HCl$, insoluble in tartaric acid (distinction from antimony, §**70**, 5d). The hydrochloric acid set free serves to hold a portion of the bismuth in solution. The presence of acetic, citric, and other organic acids prevents the precipitation of solutions of bismuth salts upon further dilution with water. The washing of the precipitated oxy-salt with pure water removes more of the acid forming a salt still more basic.

$$Bi(NO_3)_3 + H_2O = BiONO_3 + 2HNO_3$$
$$12BiONO_3 + H_2O = 6Bi_2O_3{,}5N_2O_5 + 2HNO_3$$

This is prevented by the presence of one part ammonium nitrate to five hundred parts water (Lowe, *J. pr.*, 1858, **74**, 341).

Bismuth nitrate crystallizes with ten molecules of water, $Bi(NO_3)_3.10H_2O$. It is decomposed by a small amount of water forming the basic nitrate, $BiONO_3$; this is soluble in dilute nitric acid, when further dilution with water to any extent is possible without precipitation of the basic salt, but a drop of hydrochloric acid or a chloride causes a precipitate of the oxychloride in the diluted solution. The bromide is readily decomposed by water to **BiOBr**; the iodide is stable to cold water, but is decomposed by hot water to **BiOI** (Schneider, *A. Ch.*, 1857 (3), **50**, 488); the normal sulphate very readily absorbs water to form $Bi_2(SO_4)_3.3H_2O$, which is decomposed by more water to $Bi_2O_3.SO_3$.

6. **Reactions.** *a.*—The alkali **hydroxides** precipitate from solutions of bismuth salts *bismuth hydroxide*, $Bi(OH)_3$, white; insoluble in excess of the fixed alkalis (distinction from **Sb** and **Sn**), insoluble in ammonium

* Lowe (*C. N.*, 1882, **45**, 296) dissolves the hydroxides of copper and bismuth in glycerol, adds glucose and gently warms. The copper is completely precipitated and separated from the bismuth. Upon boiling the filtrate for some time the bismuth is completely precipitated as the metal.

hydroxide (distinction from **Cu** and **Cd**). The hydroxide is converted by boiling into the oxide, Bi_2O_3, yellowish white. The precipitation is prevented by the presence of tartaric acid, citric acid, glycerol, and certain other organic substances (Köhler, *J. C.*, 1886, **50**, 428).

The alkali **carbonates** precipitate basic bismuth carbonate, $Bi_2O_3.CO_2$, white, insoluble in excess of the reagent. Freshly precipitated barium carbonate forms the same precipitate without heating.

b.—**Oxalic acid** and soluble **oxalates** precipitate *bismuth oxalate*, $Bi_2(C_2O_4)_3$, white, soluble in moderately dilute acids. Potassium **cyanide** forms a white crystalline precipitate insoluble in excess of the reagent but soluble in nitric or hydrochloric acid. Potassium **ferrocyanide** forms a yellowish white precipitate, potassium **ferricyanide** a brownish yellow, both soluble in hydrochloric acid.

c.—The action of **nitric** acid upon bismuth and its salts is fully explained under (5). *d.*—Metallic bismuth is precipitated when bismuth salts are warmed with hypophosphorous acid (separation from **Zn** and **Cd**) (Muthmann and Mawron, *Z.*, 1874, **13**, 209). From solutions of bismuth nitrate (5*d*) phosphoric acid and soluble phosphates precipitate bismuth phosphate, $BiPO_4$, white, readily soluble in **HCl**; from solutions of the chloride, diluted as much as possible without precipitation, phosphoric acid gives no precipitate, but the precipitate of the phosphate (soluble in **HCl**) is obtained with soluble phosphates.

e.—**Hydrosulphuric acid** and **sulphides** precipitate *bismuth sulphide*, Bi_2S_3, black, insoluble in dilute acids and in alkali hydroxides; insoluble in alkali sulphides (distinction from the metals of the tin group) and in alkali cyanides (distinction from copper). It is soluble by moderately concentrated nitric acid (distinction from mercury), the sulphur mostly remaining free.

Sodium thiosulphate when warmed with solutions of bismuth salts precipitates *bismuth sulphide*. **Sulphuric acid** does not precipitate solutions of bismuth chloride or nitrate. Potassium sulphate gives a precipitate with solutions of both, that with the chloride being apparently caused by the dilution of the solution.

f.—**Hydrochloric acid** and soluble **chlorides** form a precipitate of bismuth oxy-chloride, **BiOCl**, in solutions of bismuth nitrate not containing too much free nitric acid. This makes it possible for bismuth to be precipitated with the silver group salts (§**63**, 6*b*). The precipitate is readily dissolved on addition of more hydrochloric or nitric acid (distinction from the silver group chlorides).

Hydrobromic acid and soluble **bromides** do not precipitate solutions of bismuth chloride, but do precipitate solutions of the nitrate, forming the oxybromide, **BiOBr**, white. The presence of potassium bromide prevents the precipitation of a bismuth chloride solution by water and also dissolves the oxychloride which has been precipitated by the addition of water.

Hydriodic acid and soluble **iodides** precipitate from solutions of bismuth salts, unless strongly acid, bismuth iodide, black or brownish gray crystals, quite readily soluble in excess of the reagent * or in strong **HCl** without warm-

* Bismuth iodide dissolves in solution of potassium iodide with an intense yellow color, delicate to one-millionth (Stone *J. Soc. Chem. Ind.*, 1887, **6**, 416). The potassium iodide solution of bismuth iodide is used as Dragendorff's reagent to detect the presence of an alkaloid. Leger (*Bl.*, 1888, **50**, 91) uses cinchonine and potassium iodide to prove the presence of bismuth. Delicate to one-five hundred thousandth. Other metals must be removed.

ing. It is reprecipitated on diluting the solution with water. Bismuth iodide is scarcely at all decomposed by washing with cold water, but on boiling with water it is decomposed into bismuth oxy-iodide, **BiOI**, red, insoluble in **KI**, soluble in **HCl**, and in **HI** (Gott and Muir, *J. C.*, 1888, **53**, 137).

Chloric acid dissolves bismuth hydroxide, but the compound decomposes upon evaporation (Wachter, *A.*, 1844, **52**, 233). Potassium bromate and iodate both precipitate solutions of bismuth nitrate. The iodate formed is scarcely soluble, the bromate easily soluble in HNO_3.

g.—Potassium or sodium **stannite** hot, when added in excess to bismuth solutions, cause a black precipitate, from reduction to metallic bismuth, a very delicate reaction.* The stannite is made, when wanted, by adding to a stannous chloride solution, in a test-tube, enough sodium or potassium hydroxide to redissolve the precipitate at first formed: $2BiCl_3 + 3K_2SnO_2 + 6KOH = 2Bi + 6KCl + 3K_2SnO_3 + 3H_2O$ (Vanino and Treubert, *B.*, 1898, **31**, 1113).

h.—Solutions of bismuth salts, nearly neutral, poured into a hot solution of potassium bichromate precipitates the orange red chromate, $(BiO)_2Cr_2O_7$; but if poured into a cold solution of the neutral chromate a citron-yellow precipitate, $3Bi_2O_3.2CrO_3$, is formed. These precipitates are soluble in moderately concentrated acids, insoluble in fixed alkalis (distinction from **Pb**). The precipitate with $K_2Cr_2O_7$ is used in the quantitative determination of bismuth (9).

7. **Ignition.**—On charcoal, with sodium carbonate, before the **blow-pipe**, bismuth is readily reduced from all its compounds. The *globule* is easily fusible, brittle (distinction from lead), and gradually oxidizable under the flame, forming an *incrustation* (Bi_2O_3), orange-yellow while hot, lemon-yellow when cold, the edges bluish-white when cold. The incrustation disappears, or is driven by the reducing flame, without giving color to the outer flame. With borax or microcosmic salt, bismuth gives **beads**, faintly yellowish when hot, colorless when cold.

A mixture of equal parts cuprous iodide and sulphur forms an excellent reagent for the detection of bismuth in minerals by the use of the blow-pipe. The reagent mixed with the unknown is fused on charcoal or on a piece of aluminum sheet. A red sublimate indicates bismuth. Mercury gives a mixture of red and yellow sublimates (Hutchings, *C. N.*, 1877, **36**, 249).

Bismuth chloride may be sublimed at the temperature of boiling sulphur; recommended as a separation from lead (Remmler, *B.*, 1891, **24**, 3554).

8. **Detection.**—Bismuth is precipitated from its solutions by H_2S forming Bi_2S_3. By its insolubility in $(NH_4)_2S$ or $(NH_4)_2S_x$ and solubility in hot dilute HNO_3 it is separated with **Pb**, **Cu**, and **Cd** from the other metals of the tin and copper group. Dilute H_2SO_4 removes the lead and NH_4OH precipitates the bismuth as $Bi(OH)_3$, leaving the **Cu** and **Cd** in solution. The presence of the bismuth is confirmed by the action of a hot solution of K_2SnO_2 or **NaOH** and formaldehyde † on the white precipitate of $Bi(OH)_3$, giving metallic bismuth (6*g*) or by dissolving the $Bi(OH)_3$ in **HCl** and its precipitation as **BiOCl** upon dilution with water (5*d*).

9. **Estimation.**—(*1*) As metallic bismuth formed by fusion with potassium cyanide. (*2*) As Bi_2O_3 formed by ignition of bismuth salts of organic acids, or of the salts of volatile inorganic oxyacids. (*3*) By precipitation by H_2S, and

* For a modification of this test see Muir (J. C., 1877, **32**, 45).

† Sodium stannite reduces lead hydroxide while formaldehyde does not. Traces of lead may be present owing to imperfect separation.

after drying at 100°, weighing as Bi_2S_3. (*4*) By precipitation by $K_2Cr_2O_7$, and after drying at 120°, weighing as $(BiO)_2Cr_2O_7$. (*5*) *Volumetrically.* By precipitation with $K_2Cr_2O_7$. Dissolve the chromate in dilute acid, transfer to an azotometer and reduce the chromate with hydrogen peroxide (Baumann, *Z. angew.*, 1891, 331). (*6*) By precipitation as a phosphate with standard sodium phosphate; dilution to definite volume and determination of the excess of phosphate in an aliquot part with uranium acetate (Muir, *J. C.*, 1877, **32**, 674).

10. **Oxidation.**—Metallic bismuth reduces salts of **Hg**, **Ag**, **Pt**, and **Au** to the metallic state. Bismuth is precipitated as free metal from its solutions by **Pb**, **Sn**, **Cu**, **Cd**, **Fe**, **Al**, **Zn**, **Mg**, and HH_2PO_2 (*6d*). All salts of bismuth are oxidized to Bi_2O_5 by **Cl** or H_2O_2 in strong alkaline mixture (Hasebrock, *B.*, 1887, **20**, 213: Schiff, *A. Ch.*, 1861 (3), **63**, 474). All compounds of bismuth are reduced to the metal by potassium stannite K_2SnO_2 (*6g*). Bismuth chloride or bromide heated in a current of hydrogen is partially reduced to the free metal (Muir, *J. C.*, 1876, **29**, 144). It is precipitated as free metal upon warming in alkaline mixture with grape sugar (*5b*).

§77. Copper (Cuprum) Cu = 63.57. Valence one and two.

1. **Properties.**—*Specific gravity*, electrolytic, 8.914; melted, 8.921; natural crystals, 8.94; rolled and hammered sheet, 8.952 to 8.958 (Marchand and Scheerer, *J. pr.*, 1866, **97**, 193). *Melting point*, 1083° (*Cir. B. S.*, **35**, 1915). A red metal, but thin sheets transmit a greenish-blue light, and it also shows the same greenish-blue tint when in a molten condition. Of the metals in ordinary use, only gold and silver exceed it in malleability. In ductility it is inferior to iron and cannot be so readily drawn into exceedingly fine wire. Although it ranks next to iron in tenacity, its wire bears about half the weight which an iron wire of the same size would support. As a conductor of heat it is surpassed only by gold. Next to silver it is the best conductor of electricity. Dry air has no action upon it; in moist air it becomes coated with a film of oxide which protects it from further action of air or of water. It forms a number of very important alloys with other metals; bronze (copper and tin), brass (copper and zinc with sometimes small amounts of lead or tin), German silver (copper, nickel and zinc).

2. **Occurrence.**—Copper is found native in various parts of the world, and especially in the region of Lake Superior. It is found chiefly as sulphides in enormous quantities in Montana, Colorado, Chili and Spain; as a carbonate in Arizona. It is very widely distributed and occurs in various other forms. Chalcopyrite ($CuFeS_2$); chalcocite (Cu_2S); green malachite ($Cu_2(OH)_2CO_3$); blue malachite ($Cu_3(OH)_2(CO)_2$); cuprite (Cu_2O); and tenorite (melanconite) (**CuO**).

3. **Preparation.**—For the details of the various methods of copper-smelting and refining, the works on metallurgy should be consulted. In the laboratory pure copper may be produced (*1*) by electrolysis; (*2*) reduction by ignition in hydrogen gas; (*3*) reduction of the oxide by ignition with carbon, carbon monoxide, illuminating gas, or other forms of carbon; (*4*) reduction of the oxide by **K** or **Na** at a temperature a little above the melting point of these metals; (*5*) reduction by fusion with potassium cyanide: $CuO + KCN = Cu + KCNO$. For its reduction in the wet way, see 10.

4. **Oxides and Hydroxides.**—*Cuprous oxide* (Cu_2O), red, is found native; it is prepared: (*1*) by reducing **CuO** by means of grape-sugar in alkaline mixture; (*2*) by igniting **CuO** with metallic copper; (*3*) by treating an ammoniacal cupric solution with metallic copper; then adding **KOH** and drying. *Cuprous hydroxide*, **CuOH**, brownish yellow, is formed by precipitating cuprous salts with **KOH** or **NaOH**. *Cupric oxide*, **CuO**, black, is formed by igniting the hydroxide,

carbonate, sulphate, nitrate and some other cupric salts in the air; or by heating the metal in a current of air. *Cupric hydroxide*, $Cu(OH)_2$, is formed by precipitating cupric salts with **KOH** or **NaOH**. It is stated by Rose (*Pogg.*, 1863, **120**, 1) that *tetracupric monoxide*, Cu_4O, is formed by treating a cupric salt with **KOH** and a quantity of K_2SnO_2 insufficient to reduce it to the metallic state. A *peroxide* of copper, CuO_2, is supposed to be formed by treating $Cu(OH)_2$ with H_2O_2 at 0° (Krüss, *B.*, 1884, **17**, 2593). (§10.)

5. **Solubilities.**—*a.*—*Metal.*—Copper does not readily dissolve in acids with evolution of hydrogen; it dissolves most readily in nitric acid chiefly with evolution of nitric oxide: $3Cu + 8HNO_3 = 3Cu(NO_3)_2 + 4H_2O + 2NO$ (Freer and Higley, *Am.*, 1899, **21**, 377); also in hot concentrated sulphuric acid, with evolution of sulphurous anhydride: $Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2$. If dry hydrochloric acid gas be passed over heated copper, **CuCl** is formed with evolution of hydrogen (Weltzien, *A. Ch.*, 1865, (4), **6**, 487). A saturated solution of hydrochloric acid at 15° dissolves copper as **CuCl** with evolution of hydrogen. The action is very rapid if the copper be first immersed in a platinum chloride solution. Heat favors the reaction and the presence of $10H_2O$ to one **HCl** prevents the action (Engel, *C. r.*, 1895, **121**, 528). Hydrobromic acid concentrated acts slowly in the cold and rapidly when warmed, forming $CuBr_2$, with evolution of hydrogen. Cold hydriodic acid, in absence of iodine, is without action (Mensel, *B.*, 1870, **3**, 123). Ammonium sulphide, $(NH_4)_2S$, colorless, acts upon copper turnings with evolution of hydrogen, forming Cu_2S (Heumann, *J. C.*, 1873, **26**, 1105).

b.—*Oxides.*—*Cuprous oxide* and *hydroxide* are insoluble in water, soluble in hydrochloric acid with formation of cuprous chloride, white, unstable, readily oxidized by the air to colored cupric salts. *Cupric oxide*, black, and *hydroxide*, blue, are insoluble in water, soluble in dilute acids; in a mixture of equal parts glycerine and sodium hydroxide, sp. gr. 1.20 (separation from **Cd**) (Donath, *J. C.*, 1879, **36**, 178), in a mixture of tartrates and fixed alkalis (but precipitated as Cu_2O by heating with glucose) (separation from **Cd** and **Zn**) (Warren, *C. N.*, 1891, **63**, 193); insoluble in ammonium hydroxide in absence of ammonium salts (Maumene, *J. C.*, 1882, **42**, 1266).

c.—*Salts.*—All salts of copper, except the sulphides, are soluble in ammonium hydroxide. All cuprous salts are insoluble in water, soluble in hydrochloric acid and reprecipitated upon addition of water. They are readily oxidized to cupric salts on exposure to moist air. Cuprous chloride and bromide are soluble in ammonium chloride solution (Mohr, *J. C.*, 1874, **27**, 1099). Cupric salts, in crystals or solution, have a green or **blue color**; the chloride (2 *aq.*) in solution is emerald-green when concentrated, light blue when dilute; the sulphate (5 *aq.*) is "blue vitriol." Anhydrous cupric salts are white. The crystallized chloride and chlorate are **deliquescent**; the sulphate, permanent; the acetate, efflorescent. Cupric basic carbonate, oxalate, phosphate, borate, arsenite, sulphide, cyanide, ferrocyanide, ferricyanide, and tartrate are **insoluble** in water. The ammonio salts, the potassium and sodium cyanides, and the potassium and sodium tartrate, are soluble in water. In alcohol the sulphate and acetate are insoluble; the chloride and nitrate, soluble. Ether dissolves the chloride.

6. **Reactions.**—*a.*—**Fixed alkali hydroxides** precipitate acid solutions of cuprous chloride, first as the white cuprous chloride, changing with more of the alkali to the yellow *cuprous hydroxide*, insoluble in excess. **Ammonium hydroxide** and **carbonate** precipitate and redissolve the hydroxide to a colorless solution, which turns blue on exposure. The colorless ammoniacal solution is precipitated by potassium hydroxide. **Fixed alkali carbonates** precipitate the yellow *cuprous carbonate*, Cu_2CO_3.

Fixed alkalis—**KOH**—added *to saturation* in solutions of cupric salts, precipitate *cupric hydroxide*, $Cu(OH)_2$, deep blue, insoluble in excess unless concentrated (Loew, *Z.*, 1870, **9**, 463), soluble in ammonium hydroxide (if too much fixed alkali is not present), very soluble in acids, and changed, by standing, to the black compound, $Cu_3O_2(OH)_2$; by boiling, to CuO. If tartaric acid, citric acid, grape-sugar, milk-sugar, or certain other **organic** substances are present, the precipitate either does not form at all, or redissolves in excess of the fixed alkali to a blue solution. The alkaline tartrate solution may be boiled without change; in presence of glucose, the application of heat causes the precipitation of the yellow cuprous oxide. Alkali hydroxides, *short of saturation*, form insoluble basic salts, of a lighter blue than the hydroxide.

Ammonium hydroxide added short of saturation precipitates the pale blue basic salts; added just to saturation, the deep blue hydroxide (in both cases *like the fixed alkalis*); added to supersaturation, the precipitate dissolves to an intensely deep blue solution (separation from bismuth). The blue solution is a cuprammonium compound, not formed unless ammonium salts be present. It has been isolated as $CuSO_4.(NH_3)_4$ (§77, 5*b*). The deep blue solution probably consists of this compound in a hydrated condition, *i. e.* $Cu(OH)_2.2NH_4OH.(NH_4)_2SO_4$; or $(NH_4)_4Cu(OH)_4SO_4$. Other salts than the sulphate form the corresponding compounds: $CuCl_2 + 4NH_4OH = Cu(OH)_2.2NH_4OH.2NH_4Cl$. The blue color with ammonium hydroxide is a good test for the presence of copper in all but traces (one to 25,000), its sensitiveness is diminished by the presence of iron (Wagner, *Z.*, 1881, **20**, 351). **Ammonium carbonate**, like ammonium hydroxide, precipitates and redissolves to a blue solution. **Carbonates** of **fixed alkali** metals—as K_2CO_3—precipitate the greenish-blue, basic *carbonate*, $Cu_2(OH)_2CO_3$, of variable composition, according to conditions, and converted by boiling to the black, basic hydroxide and finally to the black oxide. Barium carbonate precipitates completely, on boiling, a basic carbonate.

From the blue ammoniacal solutions a concentrated solution of a **fixed alkali** precipitates the blue hydroxide, changed on boiling to the black oxide, CuO.

b.—**Oxalates, cyanides, ferrocyanides, ferricyanides** and **thiocyanates** precipitate their respective cuprous salts from cuprous solutions not too strongly acid. The ferricyanide is brownish-red, the others are white. The thiocyanate is used to separate copper from palladium (Wöhler, *A. Ch.*, 1867, (4), **10**, 510); and also from cadmium. In solutions of cupric salts, **oxalates** precipitate *cupric*

oxalate, CuC_2O_4, bluish-white, insoluble in acetic acid, and formed from mineral acid salts of copper by oxalic acid added with alkali acetates.

Potassium cyanide forms a brownish precipitate of *cupric cyanide*, $Cu(CN)_2$, which immediately changes to the yellowish green *cupric cuprous cyanide* with the evolution of cyanogen. On warming, this precipitate changes to the white *cuprous cyanide*, $Cu_2(CN)_2$, with further evolution of cyanogen. Excess of potassium cyanide dissolves the precipitate with the formation of the double cuprous salt, $K_3Cu(CN)_4$, or, in the presence of a smaller excess of potassium cyanide, $K_2Cu(CN)_3$. (Kunschert, *Z.* Anorg., **41**, 359, 1904). The potassium cyanide also dissolves cupric oxide, hydroxide, carbonate, *sulphide*, etc., changing rapidly to the double cuprous cyanide in solution in the alkali cyanide. Hydrogen sulphide does not precipitate the copper from solutions of copper salts in potassium cyanide on account of the very slight concentration of the copper ions in such solutions (5.10^{-29}. Kunschert, *ibid.*). This serves as a separation from Cadmium which is precipitated by hydrogen sulphide from a potassium cyanide solution. **Potassium ferrocyanide** precipitates *cupric ferrocyanide*, $Cu_2Fe(CN)_6$, reddish-brown, insoluble in acids, decomposed by alkalis; a very delicate test for copper (1 to 200,000); forming in highly dilute solutions a reddish coloration (Wagner, *Z.*, 1881, **20**, 351). **Potassium ferricyanide** precipitates *cupric ferricyanide*, $Cu_3(Fe(CN)_6)_2$, yellowish-green, insoluble in hydrochloric acid.

Potassium thiocyanate, with cupric salts, forms a mixed precipitate of cuprous thiocyanate, white, and a black precipitate of cupric thiocyanate, which gradually changes to the white cuprous compound, soluble in NH_4OH; in the presence of hypophosphorous or sulphurous acid the cuprous thiocyanate is precipitated at once (distinction from cadmium and zinc) (Hutchinson, *J. C.*, 1880, **38**, 748). **Ammonium benzoate** (10 per cent solution) precipitates copper salts completely from solutions slightly acidified (separation from cadmium) (Gucci, *B.*, 1884, **17**, 2659).

If to a solution of cupric salt slightly acidulated with hydrochloric acid, an excess of a solution of **nitroso-B-naphthol** in 50 per cent acetic acid be added, the copper will be completely precipitated on allowing to stand a short time (separation from **Pb**, **Cd**, **Hg**, **Mn**, and **Zn**) (Knorre, *B.*, 1887, **20**, 283).

Potassium xanthate gives with very dilute solutions of copper salt a yellow coloration; according to Wagner (*l. c.*) one part copper in 900,000 parts water may be detected.

c.—**Nitric acid** rapidly oxidizes cuprous salts to cupric salts. *d.*—A solution of cupric sulphate slightly acidulated with hydrochloric acid is precipitated as cuprous chloride by **sodium hypophosphite** (Cavazzi, *Gazzetta*, 1886, **16**, 167); if the slightly acidulated copper salt solution be boiled with an excess of the hypophosphite the copper is completely precipitated as the metal. **Sodium phosphate**, Na_2HPO_4, gives a bluish-white precipitate of copper acid phosphate, $CuHPO_4$, if the reagent be in excess and $Cu_3(PO_4)_2$ if the copper salt be in excess. **Sodium pyrophosphate** precipitates cupric salts, but not if tartrates or thiosulphates be present (separation from cadmium) (Vortmann, *B.*, 1888, **21**, 1103).

e.—Cuprous salts (obtained by treating cupric salts with $SnCl_2$) when boiled with precipitated **sulphur** deposit the copper as Cu_2S (separation from cadmium) (Orlowski, *J. C.*, 1882, **42**, 1232). Cuprous salts are precipitated or trans-

posed by **hydrosulphuric acid** or soluble **sulphides**, forming cuprous sulphide,* Cu_2S, black, possessing the same solubilities as cupric sulphide.

With cupric salts H_2S gives **CuS**, black (with some Cu_2S), produced alike in acid solutions (distinction from iron, manganese, cobalt, nickel) and in alkaline solutions (distinction from arsenic, antimony, tin).—Solutions containing only the one-hundred-thousandth of copper salt are colored brownish by the reagent. The precipitate, **CuS**, is easily soluble by nitric acid (distinction from mercuric sulphide); with difficulty soluble by strong hydrochloric acid (distinction from antimony); insoluble in hot dilute sulphuric acid (distinction from cadmium); insoluble in fixed alkali sulphides and ammonium monosulphide, but slightly soluble in ammonium polysulphide and fixed alkali. (Rössing, *Z.*, **41**, 1)† (distinction from arsenic, antimony, tin); soluble in solution of potassium cyanide (distinction from lead, bismuth, cadmium, mercury).

According to Noyes (*J. Am. Soc.* **29**, 170) 5 to 10 mg. of copper may dissolve in *ammonium polysulphide* when a large amount of copper is present.

Concerning the formation of a *colloidal cupric sulphide*, see Spring (*B.*, 1883, **16**, 1142). According to Brauner (*C. N.*, 1896, **74**, 99) cupric salts with excess of hydrogen sulphide always yield a very appreciable amount of cuprous sulphide. See also Ditte (*C. r.*, 1884, **98**, 1492). Solutions of cupric salts are reduced to cuprous salts by boiling with **sulphurous acid** (Kohner, *C. C.*, 1886, 813). **Sodium thiosulphate** added to hot solutions of copper salts gives a black precipitate of cuprous sulphide. In solutions acidulated with hydrochloric acid, this is a separation from cadmium (Vortmann, *M.*, 1888, **9**, 165); in acetic acid solution, separation from cadmium and zinc (Dovath, *Z.*, **40**, 141).

f.—**Hydrobromic acid** added to cupric solutions and concentrated by evaporation gives a rose-red color. Delicate to 0.001 m. g. (Endemann and Prochazka, *C. N.*, 1880, **42**, 8). Of the common metals only iron interferes. Potassium bromide and sulphuric acid may be used instead of hydrobromic acid.

Hydriodic acid and soluble **iodides** precipitate, from concentrated solutions of *copper* salts, *cuprous iodide*, **CuI**, white, colored dark brown by the *iodine* separated in the reaction ‡ (*a*). The iodine dissolves with color in excess of the reagent, or dissolves colorless on adding ferrous sulphate or soluble sulphites, by entering into combination. Cuprous iodide dissolves in thiosulphates (with combination).

The cuprous iodide is precipitated, free from iodine, and more com-

* Freshly precipitated cuprous sulphide transposes silver nitrate forming silver sulphide, metallic silver and cupric nitrate; with cupric sulphide, silver sulphide and cupric nitrate are formed (Schneider, *Pogg.*, 1874, **152**, 471). Freshly precipitated **sulphides** of **Fe, Co, Zn, Cd, Pb, Bi, Sn''**, and **Sn^{IV}**, when boiled with **CuCl** in presence of **NaCl** give Cu_2S and chloride of the metal: with $CuCl_2$, **CuS** and a chloride of the metal are formed, except that **SnS** gives Cu_2S, **CuCl** and **Sn^{IV}** (Raschig, *B.*, 1884, **17**, 697).

† Thio salts having the formulas $(NH_4)_2Cu_2S_7$ and $Na_2Cu_2S_7$ are formed (Rössing, *Z. anorg.* **25**, 407.)

‡ The precipitation is incomplete unless the free iodine, one of the products of the reaction, is removed by means of a reducing agent (§44).

pletely, by adding *reducing agents* with iodides; as, Na_2SO_3, H_2SO_3, $FeSO_4$ (*b*).

(*a*) $2CuSO_4 + 4KI = 2CuI + I_2 + 2K_2SO_4$

(*b*) $2CuSO_4 + 2KI + 2FeSO_4 = 2CuI + K_2SO_4 + Fe_2(SO_4)_3$

$2CuSO_4 + 4KI + H_2SO_3 + H_2O = 2CuI + 2K_2SO_4 + H_2SO_4 + 2HI$

g.—**Arsenites**, as $KAsO_2$, or arsenous acid with just sufficient alkali hydroxide to neutralize it, precipitate from solutions of cupric salts (not the acetate) the green *copper arsenite*, chiefly $CuHAsO_3$ (Scheele's green, "Paris green"), readily soluble in acids and in ammonium hydroxide, decomposed by strong potassium hydroxide solution. From cupric **acetate**, arsenites precipitate, on boiling, *copper aceto-arsenite*, $(CuOAs_2O_3)_3Cu(C_2H_3O_2)_2$, Schweinfurt green or Imperial green, "Paris green," dissolved by ammonium hydroxide and by acids, decomposed by fixed alkalis.

Soluble **arsenates** precipitate from solutions of cupric salts *cupric arsenate*, bluish-green, readily soluble in acids and in ammonium hydroxide.

h.—**Potassium bichromate** does not precipitate solutions of cupric salts: normal potassium chromate forms a brownish-red precipitate, soluble in ammonium hydroxide to a green solution, soluble in dilute acids.

7. **Ignition.**—Ignition with sodium carbonate on charcoal leaves metallic copper in finely divided grains. The particles are gathered by triturating the charcoal mass in a small mortar, with the repeated addition and decantation of water until the copper subsides clean. It is recognized by its color, and its softness under the knife. Copper readily dissolves, from its compounds in **beads** of borax and of microcosmic salt, in the outer flame of the blow-pipe. The beads are green while hot, and *blue* when cold. In the inner flame the borax bead becomes colorless when hot; the microcosmic salt turns dark green when hot, both having a reddish-brown tint when cold (Cu_2O) (helped by adding tin). Compounds of copper, heated in the inner flame, **color the outer flame** green. Addition of hydrochloric acid increases the delicacy of the reaction, giving a greenish-blue color to the flame.

8. **Detection.**—Copper is precipitated from its solutions by H_2S, forming **CuS**. By its insolubility in $(NH_4)_2S_x$ and solubility in hot dilute HNO_3 it is separated with **Pb**, **Bi**, and **Cd** from the remaining metals of the tin and copper group. Dilute H_2SO_4 with C_2H_5OH removes the lead and ammonium hydroxide precipitates the bismuth as $Bi(OH)_3$, leaving the **Cu** and **Cd** in solution. The presence of the **Cu** is indicated by the blue color of the ammoniacal solution, by its precipitation as the brown ferrocyanide after acidulation with **HCl** (*6b*); and by its reduction to **Cu°** with **Fe°**, from its neutral or acidulated solutions (10). Study the text on reactions (6) and §**102** and §**103**.

9. **Estimation.**—(*1*) It is precipitated on platinum by the electric current and weighed as the metal, or by means of zinc, the excess of zinc being dissolved by dilute hydrochloric acid. (*2*) It is converted into **CuO** and weighed after ignition, or the oxide is reduced to the metal in an atmosphere of hydrogen and weighed as such. (*3*) It may be precipitated either by H_2S or $Na_2S_2O_3$, and, after adding free sulphur and igniting in hydrogen gas, weighed as cuprous sulphide, or it may be precipitated by **KCNS** in presence of H_2SO_3 or H_3PO_2, and, after adding **S**, ignited in **H** and weighed as Cu_2S. Cu_2O, **CuO**, $Cu(NO_3)_2$, $CuCO_3$, $CuSO_4$ and many other cupric salts, are converted into Cu_2S by adding **S** and igniting in hydrogen gas. (*4*) By adding **KI** to the cupric salt and titrating the liberated **I** by $Na_2S_2O_3$; not permissible with acid radicals which oxidize **HI**. (*5*) By precipitation as **CuI** and weighing after drying at 150° (Browning,

Am. S., 1893 [3], **46**, 280). (*6*) By titrating in concentrated **HBr**, using a solution of $SnCl_2$ in concentrated **HCl**; the end reaction is sharper than with $SnCl_2$ alone (Etard and Lebeau, *C. r.*, 1890, **110**, 408). (*7*) By titration with Na_2S. Zinc does not interfere (Borntträger, *Z. angew.*, 1893, 517). (*8*) By reduction with SO_2 and precipitation with excess of standard NH_4CNS; dilution to definite volume and titration of the excess of NH_4CNS in an aliquot part, with $AgNO_3$ (Volhard, *A.*, 1878, **190**, 51). (*9*) Small amounts are treated with an excess of NH_4OH and estimated colorimetrically by comparing with standard tubes.

10. **Oxidation.**—Solutions of **Cu″** and **Cu′** are reduced to the metallic state by **Zn**, **Cd**, **Sn**, **Al**, **Pb**, **Fe**, **Co**, **Ni**, **Bi**, **Mg** *, **P**, and in presence of **KOH** by K_2SnO_2. A bright strip of iron in solution of cupric salts acidulated with hydrochloric acid, receives a bright copper coating, recognizable from solutions in 120,000 parts of water. With a zinc-platinum couple the copper is precipitated on the platinum and its presence can be confirmed by the use of H_2SO_4, concentrated, and **KBr**, an intense violet color is obtained (Creste, *J. C.*, 1877, **31**, 803). **Cu″** is reduced to **Cu′** by **Cu°** (Boettger, *J. C.*, 1878, **34**, 113), by $SnCl_2$ in presence of **HCl**, in presence of **KOH** by As_2O_3 and grape sugar, by **HI**, and by SO_2. Metallic copper is oxidized to **Cu″** by solutions of **Hg″**, **Hg′**, **Ag′**, Pt^{IV}, and **Au‴**, these salts being reduced to the metallic state. Ferric iron is reduced to the ferrous condition (Hunt, *Am. S.*, 1870, **99**, 153). Copper is also oxidized by many acids.

§78. Cadmium. Cd = 112.4. Valence two.

1. **Properties.**—*Specific gravity*, liquid, 7.989; cooled, 8.67; hammered, 8.6944. *Melting point*, 320.9° (*Cir. B. S.*, **35**, 1915). *Boiling point*, 763° to 772° (Carnelley and Williams, *J. C.*, 1878, **33**, 284). *Specific heat* is 0.0567. *Vapor density* (**H** = 1), 55.8 (Deville and Troost, *A. Ch.*, 1860, (3), **58**, 257). From these data the gaseous molecule of cadmium is seen to consist of one atom (Richter, *Anorg. Chem.*, 1893, 363). It is a white crystalline metal, soft, but harder than tin or zinc; more tenacious than tin; malleable and very ductile, can easily be rolled out into foil or drawn into fine wire, but at 80° it is brittle. Upon bending it gives the same creaking sound as tin. It may be completely distilled in a current of hydrogen above 800°, forming silver white crystals (Kämmerer, *B.*, 1874, **7**, 1724). Only slightly tarnished by air and water at ordinary temperatures. When ignited burns to **CdO**. When heated it combines directly with **Cl**, **Br**, **I**, **P**, **S**, **Se**, and **Te**. It forms many useful alloys having low melting-points.

2. **Occurrence.**—Found as greenockite (**CdS**) in Greenland, Scotland and Pennsylvania; also to the extent of one to three per cent in many zinc ores.

3. **Preparation.**—Reduced by carbon and separated from zinc (approximately) by distillation, the cadmium being more volatile. It may be reduced by fusion with **H**, **CO**, or coal gas.

4. **Oxide** and **Hydroxide.**—Cadmium forms but one *oxide*, **CdO**, either by burning the metal in air or by ignition of the hydroxide, carbonate, nitrate, oxalate, etc. It is a brownish-yellow powder, absorbs CO_2 from the air, becoming white (Gmelin-Kraut, **3**, 64). The *hydroxide* $\cdot Cd(OH)_2$ is formed by the action of the fixed alkalis upon the soluble cadmium salts; it absorbs CO_2 from the air.

5. **Solubilities.**—*a.*—*Metal.*—Cadmium dissolves slowly in hot, moderately dilute hydrochloric or sulphuric acid with evolution of hydrogen; much more

*Warren, *C. N.*, 1895, **71**, 92.

readily in nitric acid with generation of nitrogen oxides. It is soluble in ammonium nitrate without evolution of gas; cadmium nitrate and ammonium nitrite are formed (Morin, *C. r.*, 1885, **100**, 1497). *b.*—The *oxide* and *hydroxide* are insoluble in water and the fixed alkalis, soluble in ammonium hydroxide, readily soluble in acids forming salts; soluble in a cold mixture of fixed alkali and alkali tartrate, reprecipitated upon boiling (distinction from copper) (Behal, *J. Pharm.*, 1885, (5), **11**, 553). *c.*—**Salts.**—The sulphide, carbonate, oxalate, phosphate, cyanide, ferrocyanide and ferricyanide are insoluble (§27) in water, soluble in hydrochloric and nitric acids, and soluble in NH_4OH, except **CdS**. The chloride and bromide are *deliquescent*, the iodide is permanent; they are soluble in water and alcohol.

6. **Reactions.** *a.*—The **fixed alkali hydroxides**—in absence of tartaric and citric acids, and certain other organic substances—precipitate, from solutions of cadmium salts, cadmium hydroxide, $Cd(OH)_2$, white, insoluble in excess of the reagents (distinction from tin and zinc). **Ammonium hydroxide** forms the same precipitate which dissolves in excess. If the concentrated cadmium salts be dissolved in excess of ammonium hydroxide with gentle heat and the solution then cooled, crystals of the salt, with variable amounts of ammonia, are obtained; *e. g.*, $CdCl_2(NH_3)_3$, $CdSO_4(NH_3)_4$, $Cd(NO_3)_2(NH_3)_6$ (Andre, *C. r.*, 1887, **104**, 908 and 987; Kwasnik, *Arch. Pharm.*, 1891, **229**, 569). The **fixed alkali carbonates** precipitate cadmium carbonate, $CdCO_3$, white, insoluble in excess of the reagent, **ammonium carbonate** forms the same precipitate dissolving in excess. Barium carbonate, in the cold, completely precipitates cadmium salts as the carbonate.

b.—**Oxalic acid** and **oxalates** precipitate cadmium oxalate, white, soluble in mineral acids and ammonium hydroxide. **Potassium cyanide** precipitates cadmium cyanide, white, soluble in excess of the reagent as $Cd(CN)_2.2KCN$; **ferrocyanides** form a white precipitate; **ferricyanides** a yellow precipitate, both soluble in hydrochloric acid, and in ammonium hydroxide. **Potassium sulphocyanate** does not precipitate cadmium salts (distinction from copper). Cadmium salts in presence of **tartaric acid** are not precipitated by fixed alkali hydroxides in the cold; on boiling, cadmium oxide is precipitated (separation from copper and zinc) (Aubel and Ramdohr, *A. Ch.*, 1858, (3), **52**, 109). *c.*—**Nitric acid** dissolves all the known compounds of cadmium. *d.*—Soluble **phosphates** precipitate *cadmium phosphate*, white, readily soluble in acids. **Sodium pyrophosphate** precipitates cadmium salts, soluble in excess and in mineral acids, not in dilute acetic. The reaction is not hindered by the presence of tartrates or of thiosulphates (separation from **Cu**) (Vortmann, *B.*, 1888, **21**, 1104).

e.—**Hydrogen sulphide** and soluble **sulphides** precipitate, from solutions neutral, alkaline, or not too strongly acid, cadmium sulphide, yellow; insoluble in excess of the precipitant (Fresenius, *Z.*, 1881, **20**, 236), in ammonium hydroxide, or in cyanides (distinction from copper); soluble in hot dilute sulphuric acid and in a saturated solution of sodium chloride * (distinction from copper) (Cushman, *Am.*, 1896, **17**, 379).

*Owing to the formation of incompletely-dissociated $CdCl_2$. CdI_2 is still less dissociated and accordingly **CdS** dissolves more readily in **HI** than in **HCl** and much more readily than in HNO_3 of the same concentration. On the other hand, of course, precipitation of the sulphide takes place with more difficulty from the iodide than from the other salts.

Sodium thiosulphate, $Na_2S_2O_3$, does not precipitate solutions of cadmium salts (Follenius, *Z.*, 1874, **13**, 438), but in excess of this reagent, ammonium salts being absent, sodium carbonate completely precipitates the cadmium as carbonate (distinction from copper) (Wells, *C. N.*, 1891, **64**, 294). Cadmium salts with excess of sodium thiosulphate are not precipitated upon boiling with hydrochloric acid (distinction from copper) (Orlowski, *J. C.*, 1882, **42**, 1232). *f.*—The non-precipitation by **iodides** is a distinction from copper. *g.*—Soluble **arsenites** and **arsenates** precipitate the corresponding cadmium salts, readily soluble in acids and in ammonium hydroxide. *h.*—Alkali **chromates** precipitate yellow cadmium chromate from concentrated solutions only, and soluble on addition of water.

i.—A solution of copper and cadmium salts, very dilute, when allowed to spread upon a filter paper or porous porcelain plate, gives a ring of the cadmium salt beyond that of the copper salt, easily detected by hydrogen sulphide (Bagley, *J. C.*, 1878, **33**, 304).

7. **Ignition.**—On charcoal, with sodium carbonate, cadmium salts are reduced by the blow-pipe to the metal, which is usually vaporized and reoxidized nearly as fast as reduced, thereby forming a characteristic brown incrustation (**CdO**). This is volatile by reduction only, being driven with the reducing flame. Cadmium oxide colors the borax bead yellowish while hot, colorless when cold; microcosmic salt, the same. If fused with a bead of K_2S, a yellow precipitate of **CdS** is obtained (distinction from zinc) (Chapman, *J. C.*, 1877, **31**, 490).

8. **Detection.**—Cadmium is precipitated from its solutions by H_2S forming **CdS**. By its insolubility in $(NH_4)_2S$ or $(NH_4)_2S_x$ and solubility in hot dilute HNO_3 it is separated with **Pb**, **Bi**, and **Cu** from the other metals of the second group. Dilute H_2SO_4 with C_2H_5OH removes the lead and NH_4OH precipitates the bismuth as $Bi(OH)_3$, leaving the **Cu** and **Cd** in solution. If copper be present, **KCN** is added until the solution becomes colorless, when the **Cd** is detected by the formation of the yellow **CdS** with H_2S. If **Cu** be absent the yellow **CdS** is obtained at once from the ammoniacal solution with H_2S. See also 6i.

9. **Estimation.**—(*1*) It is converted into, and after ignition weighed as an oxide. (*2*) Converted into, and after drying at 100°, weighed as **CdS**. (*3*) Precipitated as CdC_2O_4 and titrated by $KMnO_4$. (*4*) Electrolytically from a slightly ammoniacal solution of the sulphate or from the oxalate rendered acid with oxalic acid. (*5*) Separated from copper by **KI**; the **I** removed by heating; the excess of **KI** removed by KNO_2 and H_2SO_4; the cadmium precipitated by Na_2CO_3 and ignited to **CdO** (Browning, *Am. S.*, 1893, **146**, 280). (*6*) By adding a slight excess of H_2SO_4 to the oxide or salt, and evaporation first on the water bath and then on the sand bath, weighed as $CdSO_4$ (Follenius, *Z.*, 1874, **13**, 277).

10. **Oxidation.**—Metallic cadmium precipitates the free metals from solutions of **Au**, **Pt**, **Ag**, **Hg**, **Bi**, **Cu**, **Pb**, **Sn**, and **Co**; and is itself reduced by **Zn**, **Mg**, and **Al**.

§79. Comparison of Certain Reactions of Bismuth, Copper, and Cadmium.

Taken in Solutions of their Chlorides, Nitrates, Sulphates, or Acetates.

	Bi	Cu	Cd
KOH or **NaOH**, in excess	$Bi(OH)_3$, white.	$Cu(OH)_2$, dark blue.	$Cd(OH)_2$, white.
NH_4OH, in excess	$Bi(OH)_3$, white.	Blue solution.	Colorless solution.
Dilution of saturated solutions	BiOCl, white (§76, 5*d*).	.....	.....
Iodides	Partial precipitation in solutions not very strongly acid (§76, 6*f*).	Precipitation of **CuI**, with liberation of iodine (§77, 6*f*).	.....
Sulphides	Bi_2S_3, black, insoluble in **KCN**.	Cu_2S and **CuS**, black, soluble in **KCN**.	**CdS**, yellow, insoluble in **KCN**.
Iron or zinc	**Bi**, spongy precipitate.	**Cu**, bright coating (§77, 10).	**Cd**, gray sponge with zinc, no action with iron.
Glucose, **KOH**, and heat	**Bi**, black.	Cu_2O, yellow (§77, 5*b*).	.....
K_2SnO_2 + **KOH**	**Bi**, black.	**Cu**, precipitated metal.	.....

SYSTEMATIC ANALYSIS OF THE METALS OF THE TIN AND COPPER GROUP.

The precipitation of the metals of the second group (Tin and Copper Group) by hydrosulphuric acid, and their separation into Division A (Copper Group) and Division B (Tin Group). See §312.

§80. **Manipulation.**—The filtrate from Group I (§62), or the original solution, if the metals of the silver group be absent is warmed nearly to boiling and saturated with H_2S gas. The volume of the solution should be about 50 c.c. and it should contain about 6 per cent of concentrated **HCl** by volume. After passing H_2S for about 15 minutes through the hot solution, allow it to cool, dilute with an equal volume of water and again pass H_2S for some time through the cold solution. Shake well to coagulate the precipitate and filter. Pass H_2S again through the filtrate, filter and repeat until no further H_2S precipitate is obtained.

$$2H_3AsO_4 + xHCl + 5H_2S = As_2S_5 + xHCl + 8H_2O$$

or $$2H_3AsO_4 + xHCl + 5H_2S = As_2S_3 + xHCl + S_2 + 8H_2O$$

$$SnCl_4 + 2H_2S = SnS_2 + 4HCl$$

$$SnCl_2 + H_2S = SnS + 2HCl$$

$$2Bi(NO_3)_3 + 3H_2S = Bi_2S_3 + 6HNO_3$$

$$CdSO_4 + H_2S = CdS + H_2SO_4$$

§81. *Notes.—1.* Hydrosulphuric acid gas should be used in precipitating the metals of the second group. It may be generated in a Kipp apparatus, using ferrous sulphide, **FeS**, and dilute commercial sulphuric acid (1–12). Commercial hydrochloric acid may be used instead of sulphuric. The gas should

be passed through a wash bottle containing water to remove any acid that may be carried over mechanically. It should always be conducted through a capillary tube into the solution to be analyzed contained in a flask. Less gas is required and the solution is less liable to be thrown from the test tube by the excess of unabsorbed gas.

2. In treating the unknown solution with H_2S, it should be passed into the liquid until, upon shaking the flask, capped with the thumb, there is no formation of a partial vacuum due to the further absorption of the gas by the liquid.

3. H_2S is decomposed by HNO_3 or HNO_3 + **HCl** (nitrohydrochloric acid) (§257, 6*B*), hence these acids must not be present in excess. If these acids were used in preparing the solutions for analysis, they must be removed by evaporation. Sulphuric acidulation is not objectionable to precipitation with H_2S, but could not be used until absence of the metals of the calcium group (Group V.) has been assured. If this group is present strontium and especially, barium, will invariably be present in the H_2S precipitate on account of the oxidation of the sulphur to sulphuric acid. For this reason, oxidizing agents must be removed from the solution so far as possible. If ferric chloride is present, 15 milligrams of barium may be present in this precipitate as sulphate. Curtman and Frankel (*J. Am. Soc.*, **33**, 724, 1911.) For detection of the barium see §301, 5.

4. The precipitation of the silver group has left the solution acid with **HCl** and prepares the solution for precipitation with H_2S if other acids are not present in excess. A moderate excess of **HCl** is necessary to insure the precipitation of arsenic if present in the arsenic condition. For this purpose the solution must be hot and must contain at least 6 per cent by volume of concentrated **HCl**. Under these conditions the arsenic precipitates slowly (69).

The strong acid, especially when hot, prevents the precipitation of the other metals, especially tin, lead and cadmium. For this reason, the solution must be cooled and diluted and again saturated with H_2S in order to precipitate these metals. The solution must not be too largely diluted or traces of **Co**, **Ni** and **Zn** will be precipitated. About one part of **HCl** to 25 of the solution must be present to prevent the precipitation of **Zn**, and it is seldom advisable to use more than one part of **HCl** to ten of the solution * (this refers to the reagent **HCl**, §324).

5. The precipitated sulphides of the metals of the tin and copper group (second group) present a variety of colors, which aid materially in the further analysis of the group. **CdS**, SnS_2, As_2S_3, and As_2S_5 are lemon-yellow; Sb_2S_5 and Sb_2S_3 are orange; **SnS**, **HgS**, **PbS**, Bi_2S_3, Cu_2S and **CuS** are black to brownish-black. If too much **HCl** be present, lead salts frequently precipitate a red double salt of lead chloride and lead sulphide (§57, 6*c*). Mercuric chloride at first forms a white precipitate of $HgCl_2.2HgS$, changing from yellow to red, and finally to black with more H_2S, due to the gradual conversion to **HgS** (§58, 6*a*).

6. Addition of water to the solution before passing in H_2S may cause the precipitation of the oxychlorides of **Sb**, **Sn** or **Bi** (*5d*; §70, §71 and §76). These should not be redissolved by the addition of more **HCl**, as they are readily transposed to the corresponding sulphides by H_2S, and the excess of acid necessary to their resolution may prevent the precipitation of cadmium or cause the formation of the red precipitate with lead chloride.

7. The presence of a strong oxidizing agent as HNO_3, $K_2Cr_2O_7$, $FeCl_3$, etc., causes with H_2S the formation of a white precipitate of sulphur (§125, 6*c*), which is often mistaken as indicating the presence of a second group metal.

* Addition of a strong acid, containing **H** ions in large quantity, diminishes the already slight dissociation of the H_2S (§44), thus decreasing in number the **S** ions, whose concentration multiplied by that of the metal ions must equal the solubility-product of the sulphide in question, before precipitation can take place. Precipitation of some of the sulphides of the Tin and Copper Group may be entirely prevented in this way.

It frequently happens that addition of water alone will cause precipitation of these sulphides from a strongly acid solution which has been saturated with H_2S. This appears strange in view of the fact that the acid which prevented precipitation and the acid which finally produced it were both diluted by the added water in the same proportion. But as a matter of fact dilution does not have the same effect on a strong acid as on a weak one. Dissociation is always increased by dilution, but in much greater ratio in the case of a weakly-dissociated body as H_2S than where the dissociation of the substance is already practically complete, as in the case of the strong acid. Dilution in the case mentioned increases the relative concentration of the **S** ions and so the solubility-product is reached and precipitation results.

If the original solution be dark colored, it is advisable to warm with hydrochloric acid and alcohol (§125, 6*f* and 10) to effect reduction of a possible higher oxidized form of **Cr** or **Mn** before the precipitation with H_2S, thus avoiding the unnecessary precipitation of sulphur.

8. Complete precipitation of the metals of the second group with H_2S may fail: (**1**) from incomplete saturation with the gas (§81, 2); (**2**) from the presence of too much **HCl** (§81, 4); (**3**) from the presence of much pentad arsenic (§69, 6*e*). The first cause of error may be avoided by careful observance of the directions in note (2). Too much acid may be present because excess of acid had been used in dissolving the unknown. After precipitating the first group, excess of nitric should be removed by evaporating the solution nearly to dryness then diluting and adding the required amount of **HCl**. As a further precaution a portion of the filtrate from the H_2S precipitate should be diluted with several volumes of water and H_2S passed. If a precipitate is obtained, the entire solution should be diluted and saturated with H_2S. As^V must be precipitated by passing H_2S rapidly through the hot moderately acid solution before dilution as long as the slow formation of the arsenic precipitate continues.

§82. **Manipulation.**—After the precipitate has been well washed with hot water the point of the filter is pierced with a small stirring rod and the precipitate washed into a beaker, using as small an amount of water as possible. If **As**, **Sb** and **Sn** are present,* ammonium sulphide $(NH_4)_2S$ (§38, 2) is then added and the precipitate digested for several minutes with warming:

$$As_2S_3 + 2(NH_4)_2S_2 = (NH_4)_4As_2S_5 + S_2$$
$$SnS + (NH_4)_2S_2 = (NH_4)_2SnS_3$$
$$2SnS_2 + 2(NH_4)_2S_2 = 2(NH_4)_2SnS_3 + S_2$$
$$2Sb_2S_3 + 6(NH_4)_2S_2 = 4(NH_4)_3SbS_4 + S_2$$
$$2MoS_3 + 2(NH_4)_2S_2 = 2(NH_4)_2MoS_4 + S_2$$

The precipitate is then filtered and washed once or twice with a small amount of $(NH_4)_2S$, and then with hot water. The filtrate consisting of solutions of the sulphides of **As**, **Sb**, **Sn**, **Au**, **Pt**, **Mo** (*Gr*, *Ir*, *Se*, *Te*, *W*, *V*), constitutes the **Tin Group** (Division A of the second group). The precipitate remaining upon the filter, consisting of the sulphides of **Hg**, **Pb**, **Bi**, **Cu**, **Cd** (*Os*, *Pd*, *Rh*, and *Ru*), constitutes the **Copper Group** (Division B of the second group, §95).

§83. *Notes.*—1. The precipitate of the sulphides of the tin and copper group must be thoroughly washed with hot water (preferably containing H_2S and about one per cent of reagent **HCl** to prevent the formation of soluble colloidal sulphides (§69, 5*e*), to insure the removal of the metals of the iron and zinc groups, which would be precipitated on the addition of the ammonium sulphide (§144).

2. Yellow ammonium sulphide, $(NH_4)_2S_x$, forms upon allowing the normal sulphide, $(NH_4)_2S$, to stand for sometime, or it may be prepared for immediate use by adding sulphur to the freshly prepared normal sulphide (§257, 4).

* This operation is necessary only when both divisions of the group are present, and is to be avoided when *unnecessary*. Hence a little of the 2nd group precipitate is tested by warming with 1 or 2 cc. $(NH_4)_2S_x$. If it *all* dissolves, only **As**, **Sb**, **Sn** can be present; if *nothing* dissolves, none of these can be present; if *part* dissolves, then the whole 2nd group precipitate must be so treated. To see if anything has dissolved in the $(NH_4)_2S_x$ it is acidified *slightly* with **HCl** (test with litmus); a milky, white precipitate of **S** will always be formed, but if any sulphides are present they will appear as a flocculent, colored precipitate. If the whole 2nd group precipitate s treated with $(NH_4)_2S_x$, the solution is filtered and acidified just as the test portion was.

Wash the precipitate thoroughly on the filter, and then digest (in the test-tube) with **colorless ammonium sulphide**,* using as little as possible (§83, 4). Treat the **Residue**, well washed, as directed in §95. Precipitate the **Filtrate** with dilute **hydrochloric** acid and filter; examining this **Precipitate**,† when washed, for **As**, **Sb**, **Sn**, **Au**, **Pt**, **Mo**, as directed below. (For Rare Metals, see §104 and ff.)

THE TIN GROUP (Division A, Second Group).

Precipitate from the Yellow Ammonium Sulphide Solution: As_2S_3, As_2S_5, Sb_2S_5, SnS_2, Au_2S_3, PtS_2, MoS_3, S.

Treat the washed precipitate with **hydrochloric acid**, and, if it does not dissolve, add a minute fragment of **potassium chlorate**, and digest in a test-tube, till the sulphides are dissolved (or decolored). Filter out any sulphur, wash the filter with a few drops of hydrochloric acid, receiving the filtrate in an evaporating-dish. Remove the chlorine by a very gentle heat, until wet litmus-paper is not bleached by the vapor. Transfer a portion of the solution to the **Generator of a Marsh's Apparatus** (§69, 6′*a*).

Solution:‡ H_3AsO_4, $SbCl_5$, $SnCl_4$, $AuCl_3$, $PtCl_4$, Mo (oxychloride).

Place in the **Generator** sufficient **platinized zinc** (§135, *1*) and **dilute sulphuric acid**, and receive the gas in solution of **silver nitrate** (until sufficient precipitate is produced §69, 6′*a*, footnote). The contents of the generator are filtered and washed.

Residue from the Generator of the Marsh Apparatus: Sn, Au, Pt, (Sb, Zn).
Digest the residue in warm dilute **HCl** (§71, 5*a*). Filter and wash.

Residue: Au, Pt, Sb.

Gold and platinum may be detected by dissolving the residue in nitrohydrochloric acid and confirming by the usual reactions of these metals.

Solution: $SnCl_2$($ZnCl_2$).

Add a portion of this solution to a solution of **$HgCl_2$** and obtain the white precipitate of **HgCl** and the gray precipitate of **Hg°** as proof of the presence of **Sn** (§71, 6*j*).

Filtrate from the Generator of the Marsh Apparatus: Mo (colored solution of lower oxides). ($ZnSO_4$,H_2SO_4).

If molybdenum be present, the solution will be colored reddish-brown to violet. Evaporate to dryness with nitric acid, dissolve the residue in ammonium hydroxide, and add to dilute ni-

Products of Gases (AsH_3.SbH_3), Decomposed by Silver Nitrate Solution.
Filter and *wash.*

Precipitate: $SbAg_3$ (Ag)

Digest with warm reagent **hydrochloric acid** to dissolve the antimony; dilute (not enough to precipitate the antimony, §70, 5*d*) and filter from the precipitate of **AgCl** if necessary.

Solution: H_3AsO_3 ($AgNO_3$,HNO_3)

Remove the excess of silver by the addition of a soluble chloride as **NaCl** or **$CaCl_2$**, and filtration. **HCl** may be used, but an excess should be avoided (§59, 5*c*).

Preferably these metals (if present) should be removed from the original solution by boiling with $FeSO_4$ (§73, 6*h*). They are separated from each other by treating the solution with $H_2C_2O_4$ (§73, 6*b*). Obtain the "Cassius' Purple" with the gold (§73, 6*g*) and the potassium or ammonium double chloride with the platinum (§74, 6*f*).	Apply the *short method* for tin on this solution (§71, 6*i*). Also apply the same test to the original solution to determine if the tin is present in the stannous condition. If interfering metals are absent, obtain the sulphides, brown-black for **SnS** and yellow for SnS_2 (§71, 6*e*).**	tric acid, forming the nitric acid solution of ammonium molybdate (§75, 6*d*, footnote). Identify by the reactions with sodium phosphate (§75, 6*d*). Frequently the **Mo** will be present in the original solution as molybdates, when it can be detected at once by its reaction in acid solutions with phosphates.	Test a portion of the filtrate with H_2S for the orange precipitate of Sb_2S_3 § (§70, 6*e* and 8); if the precipitate is black (due to Ag_2S) proceed as follows: dilute a portion of the **HCl** solution and add one drop of **KI**. Filter off **AgI**. Pass H_2S into the filtrate for orange precipitate of Sb_2S_3. Dilute another portion with water to obtain the white precipitate of **SbOCl** (§70, 5*d*). Test the mirror and spots as directed in §69, 6′*c*.	Test the filtrate for the yellow As_2S_3 by H_2S (§69, 6*e*). Test the mirror and spots as directed in §69, 6′*c*.
Follow text at §73 and §74, 6*a*; §90, §93 and §94.	Follow text at §71, 6; §90 and §92.	Study the text especially, §75, *5*, *6*, *8* and *10*; §90 and §91.	Follow text at §69, 6′*a*, *b* and *c*; §70, 6*e*, *j* and 8; §81, 7; §86, *5* and *6*; §87 and §89.	Follow text at §69, 6, 6′, 7 and 8; §81, 5 and 8; §82; §85; §86, 5 and 6; §87 and §88.

* If copper be present, and mercury be absent, it is better to use **sodium sulphide** (§77, 6*e*; §58, 6*e*; §83, 3). If tin is present in the stannous form yellow ammonium sulphide must be used. Usually oxidizing agents are present which convert the Sn'' to Sn^{IV}.

† A white precipitate, of sulphur, will occur in any case. The presence of the metals as sulphides will be indicated by the colored precipitates unless they are present in the merest traces (§81, 6).

‡ In many cases the original solution may be tested directly with the Marsh test (§69, 6′*a*).

§ A black precipitate indicates that too much **HCl** was used, and a portion of the **AgCl** dissolved (§59, 5*c*; §87); in which case, to another portion, add one drop of a one per cent solution of **KI**, filter and add H_2S to the filtrate. The **KI** removes the traces of silver but does not precipitate the antimony.

** On account of its accuracy, brevity and extreme delicacy the following test for tin is preferred to the one above given. To the original solution which may contain all the ordinary metals add an excess of **KOH**, boil, and if a precipitate occurs filter and to the filtrate (or to the **KOH** solution if no precipitate be produced) add an ammoniacal solution of silver nitrate (one of $AgNO_3$ to sixteen of NH_4OH) and if, without warming, a black precipitate is produced tin is present. If the original solution contains Sn^{IV} instead of Sn'', add **Al** then dissolve the precipitate thus formed in **HCl** and proceed as above.

For arsenic sulphides the normal ammonium sulphide may be employed, but the sulphides of antimony are soluble with difficulty, and stannous sulphide is scarcely at all soluble in that reagent; while they are all readily soluble in the yellow polysulphide (6*e*; §69, §70 and §71).

3. Cupric sulphide, **CuS**, is sparingly soluble in the yellow ammonium sulphide and will give a grayish-black precipitate upon acidulation with **HCl**. The sulphides of the tin group are soluble in the fixed alkali sulphides, **K₂S** and **Na₂S**; cupric sulphide is insoluble in these sulphides. Mercuric sulphide, however, is much more soluble in fixed alkali sulphides than cupric sulphide is in the $(NH_4)_2S_X$. If copper be present and mercury be absent, it is recommended to use **K₂S** or **Na₂S** instead of $(NH_4)_2S_X$ for the separation of the second group of sulphides into divisions A (tin group) and B (copper group). But if **Hg″** be present, the $(NH_4)_2S_X$ should be used, and the presence or absence of *traces* of copper be determined from a portion of the filtrate from the silver group before the addition of **H₂S** (§103).

4. The sulphides dissolve more readily in the $(NH_4)_2S_X$ when the solution is warmed. An excess of the reagent is to be avoided, as the acidulation of the solution causes the precipitation of sulphur (§256, 3), which may obscure the precipitates of the sulphides present.

§85. **Manipulation.**—The solution of the sulphides in $(NH_4)_2S_X$ is carefully acidulated with hydrochloric acid:

$$2(NH_4)_2S_2 + 4HCl = 4NH_4Cl + S_2 + 2H_2S$$
$$(NH_4)_4As_2S_5 + 4HCl = As_2S_5 + 4NH_4Cl + 2H_2S$$
$$2(NH_4)_3SbS_4 + 6HCl = Sb_2S_5 + 6NH_4Cl + 3H_2S$$
$$(NH_4)_2SnS_3 + 2HCl = SnS_2 + 2NH_4Cl + H_2S$$

The precipitate obtained when the metals of the tin group are present is usually yellow or orange-yellow and is easily distinguished from a precipitate of sulphur alone (**SnS** and **MoS₃** are brownish-black). It should be well washed with hot water and then dissolved in hot **HCl** using small fragments of $KClO_3$ (§69, 6*e*) to aid in the solution:

$$2As_2S_3 + 10Cl_2 + 16H_2O = 4H_3AsO_4 + 20HCl + 3S_2$$
$$SnS_2 + 4HCl = SnCl_4 +$$
$$PtS_2 + 2Cl_2 = PtCl_4 + S_2$$

The solution is boiled (to insure removal of the chlorine (§69, 10) until it no longer bleaches litmus paper.

§86. *Notes.—1.* If the precipitate obtained is white, it probably consists of sulphur alone and indicates absence of more than traces of the metals belonging to this group (**GeS₂** is white, §111, 6).

2. Care should be taken not to use too much **HCl** in precipitating the sulphides from the $(NH_4)_2S_X$ solution, as some of the sulphides (especially **SnS₂**) are quite soluble in concentrated **HCl**.

3. It will be noticed (§85) that the lower sulphides of **Sb** and **Sn** are oxidized by the $(NH_4)_2S_X$, and are precipitated by the **HCl** as the higher sulphides **Sb₂S₅** and **SnS₂** respectively. This fact may be most readily observed by the precipitation of a solution of **SnCl₂** with **H₂S**, giving a brown precipitate of **SnS**, then dissolving this precipitate in $(NH_4)_2S_X$ and reprecipitating with **HCl** as the orange-colored **SnS₂**.

4. Hot reagent **HCl** (§324) dissolves the sulphides of tin quite readily without reduction; the sulphides of antimony, slowly forming **SbCl₃** only; and the sulphides of arsenic practically not at all, or at most only traces. The sulphides of **Au** and **Pt** are not soluble in **HCl**. **MoS₃** is soluble in hot con-

centrated **HCl**. The relative solubility of these sulphides in **HCl** is used as the basis of the following separation of **As** from **Sb** and **Sn** (§69, 6*c*, also bottom of next note, *5*).

Prec.: As_2S_5, Sb_2S_5, SnS_2. Heat for a few moments with concentrated **HCl** (sp. gr. 1.2). Expel all H_2S. Dilute a little and filter.

Residue:—As_2S_5, (S_2). Apply either of the following tests:

(1) Pour warm NH_4OH over the precipitate. Add H_2O_2 to this solution and boil. Cool and add a few cubic centimeters of NH_4Cl and a little $MgCl_2$ and obtain a white crystalline precipitate of $MgNH_4AsO_4$.

(2) Dissolve As_2S_5 in **HCl** + crystal of $KClO_3$. Boil. Make alkaline with NH_4OH, and add NH_4Cl and $MgCl_2$ as in (1).

Filtrate:—$SbCl_3$, $SnCl_4$. Boil to be sure of complete expulsion of H_2S.

Test for Sb:—Put drop of solution on silver coin. Bend piece of tin in form of ⌐¬. Touch one end to drop and other to coin outside the drop. Allow to stand for a few moments. Brown or black spot on coin is due to metallic **Sb**.

Test for Sn:—Heat solution with iron wire until reduction is complete. Filter and to filtrate add $HgCl_2$. A white precipitate of **HgCl** or a gray precipitate of **Hg** shows tin.

The precipitated sulphides of **As**, **Sb**, **Sn** are well washed with hot water and removed from the filter to a casserole by a spatula, or, if the amount is small, treated with the filter; a convenient amount of *concentrated* **HCl** (sp. gr. 1.2) is added and boiled a minute or two to expel H_2S. The sulphides of **Sb** and **Sn** are dissolved to form the chlorides $SbCl_3$ and $SnCl_4$ while the As_2S_3 is hardly attacked. Since the strong acid attacks the filter the solution is diluted a little, which should cause no reprecipitation if all H_2S was expelled, filtered, and the residue well washed. It may be either As_2S_3 and **S**, or **S** alone. A few cc. of warm NH_4OH are poured over it, the solution being passed through again if necessary. The As_2S_3 dissolves and the **S** remains. To the solution, which must be clear, add 1 or 2 cc. H_2O_2, 2 to 3 cc. NH_4Cl, and 2 to 3 cc. "magnesia mixture," which is $MgCl_2$ + NH_4Cl + NH_4OH. Cool, and let stand for a time. The As^V is precipitated as NH_4MgAsO_4, a white, crystalline precipitate exactly like NH_4MgPO_4 in appearance.

$$As_2S_5 + 16NH_4OH + 20H_2O_2 = 2(NH_4)_3AsO_4 + 5(NH_4)_2SO_4 + 28H_2O.$$

$$(NH_4)_3AsO_4 + MgCl_2 + [NH_4OH + NH_4Cl] = MgNH_4AsO_4 + 2NH_4Cl.$$

The filtrate from As_2S_3 is to be tested for **Sb** and **Sn**. For the **Sb**, place a few drops on a clean silver coin; it should produce no discoloration. A piece of tin, bent into the shape of a broad U, is now placed on the coin so that one end is in the center of the drop and the other in contact with the silver outside. Allow to stand about 5 minutes. If **Sb** is present it will be deposited as a brown spot on the silver covered by the drop, the **Sn** and **Ag** acting as a galvanic couple to reduce the **Sb** $^{\cdot\cdot\cdot}$ to metal. Another test consists in treating the solution with pure, fine **Fe** wire, the **Sb** being precipitated in black metallic form, while the **Sn** $^{\cdot\cdot\cdot\cdot}$ is merely reduced to **Sn** $^{\cdot\cdot}$ but not precipitated.

Test the rest of the solution for **Sn** by heating with fine **Fe** wire until the solution is colorless or greenish, with *no trace of yellow*, to make sure that all the **Sn** $^{\cdot\cdot\cdot\cdot}$ is reduced to **Sn** $^{\cdot\cdot}$. Ten minutes or more may be required. Filter and add the filtrate slowly (a few drops at a time), to a few cc. of ammonium molybdate, $(NH_4)_2MoO_4$ solution. A *deep* blue color or precipitate will appear if **Sn** $^{\cdot\cdot}$ is present, due to the reduction of the MoO_3 to a lower oxide. Or, instead of adding this filtrate to molybdate solution, it may be treated with $HgCl_2$, a white precipitate of **HgCl** being formed if **Sn** $^{\cdot\cdot}$ is present. Note that this is reversing the test for **Hg** $^{\cdot\cdot}$ with $SnCl_2$. The $HgCl_2$ test is most characteristic.

The precipitation of As_2S_3, unlike that of the other sulphides, is not prevented by the presence of any amount of **HCl**, however large, but, on the contrary, is aided. It may, therefore, be necessary, *after removing all other sulphides in the* N/5 **HCl** *solution*, to add several cc. of concentrated **HCl**, heat to boiling, and pass in H_2S for some time to precipitate the rest of the **As**. In the cold, H_3AsO_4 is very slowly precipitated by H_2S, but strong **HCl** and heat accelerate the reaction very much.

It is essential that the sulphides be *thoroughly* washed before treatment with **HCl**.

CuS is slightly soluble in $(NH_4)_2S_x$ and may give a coloration when the solution is acidified.

$(NH_4)_2S$, which is *colorless*, gives no precipitate of **S** upon addition of excess of acid; $(NH_4)_2S_x$, yellow, always gives more or less **S**, white and difficult to filter.

$$2(NH_4)_2S_x + 4HCl = 4NH_4Cl + 2H_2S + (x-1)S_2.$$

$$(NH_4)_2S + 2HCl = 2NH_4Cl + H_2S.$$

Make a blank test on the **Fe** wire used, to see that its solution in **HCl** gives no test for **Sn** with molybdate.

5. The sulphides of arsenic are readily soluble in ammonium carbonate (§69, 5*c*) and are thus separated from the sulphides of **Sb** and **Sn**, which are practically insoluble. The following table suggests a method of analysis based upon this property of these sulphides.

Digest the mixed sulphides with solution of ammonium carbonate and filter.

Residue: SnS_2, Sb_2S_5, (S).

Dissolve in hot **hydrochloric acid** (5*c*, §70 and §71).

Solution: $SnCl_4$, $SbCl_3$.

Treat with **zinc** and **hydrochloric acid** in Marsh's apparatus (§69, 6′*a*).

Deposit: Sn, (Sb).

Dissolve by **hydrochloric acid.**

Solution: $SnCl_2$.

(Residue, **Sb**.)

Test by **ammoniacal silver nitrate** and by **mercuric chloride** (§71, 6*i* and *j*).

Gas: SbH_3.

(Test the spots, §69, 6′*c*, *1*.)

Receive the gas in solution of **silver nitrate.** Dissolve the precipitate ($SbAg_3$) (§70, 6*j*), and test by H_2S (§87 and §89).

Solution:

$(NH_4)_3AsS_4 + (NH_4)_3AsO_4$

and

$(NH_4)_4As_2S_5 + (NH_4)_4As_2O_5$.

Precipitate by **hydrochloric acid;** filter; wash the precipitate and dissolve it by **chlorine** generated from a minute fragment of potassium chlorate and a little hydrochloric acid (§69, 5*c*).

Expel all free chlorine (note *9*, and §69, 10).

Solution: H_3AsO_4.

Apply Marsh's Test, as directed in §69, 6′*a*, testing the spots (§69, 6′*c*): receiving the gas in solution of **silver nitrate,** and testing the resulting solution (§87).

Examine the original solution, as indicated in §88, *1*.

The **arsenic** may also be identified by adding **HCl** to the ammonium carbonate solution, passing H_2S and dissolving the precipitate in a small amount of concentrated HNO_3. The arsenic will be oxidized to H_3AsO_4. Divide the solution into two parts. Cautiously neutralize one portion with

ammonia. When the solution is nearly neutral, add $AgNO_3$ and a drop or two of ammonia without shaking the solution. A reddish brown ring of Ag_3AsO_4 will form at the neutral zone of the solution. To the other portion, add magnesia mixture and ammonia until the solution is alkaline. A crystaline precipitate of $MgNH_4AsO_4$ will form on standing.

The plan above given may be varied by *separating antimony and tin by ammonium carbonate* in fully oxidized solution, as follows: The Sb_2S_5 and SnS_2 are dissolved by nitrohydrochloric acid, to obtain the antimony as pyroantimonic acid. The solution is then treated with excess of *ammonium carbonate*, in a vessel wide enough to allow the carbonic acid to escape without waste of the solution.

The soluble diammonium dihydrogen pyroantimonate, $(NH_4)_2H_2Sb_2O_7$, is formed. Meanwhile the $SnCl_4$ is fully precipitated as H_2SnO_3 (§71, 6*a*), and may be filtered out from the solution of pyroantimonate.

The liability of failure, in this mode of separating antimony and tin, lies in the non-formation of pyroantimonic acid by nitrohydrochloric acid. The ordinary antimonic acid forms a less soluble ammonium salt, but this acid is not so likely to occur in obtaining the solution with nitrohydrochloric as *antimonous chloride*, $SbCl_3$. Excess of ammonium carbonate does not redissolve the Sb_2O_3 which it precipitates from $SbCl_3$, as stated in §70, 6*a*.

The above plan may also be varied as follows: After removal of the arsenic sulphide with $(NH_4)_2CO_3$, the residue is dissolved in strong HCl, not using $KClO_3$ or HNO_3. The solution consists of $SnCl_4$ and $SbCl_3$. Divide in two portions: (*1*) Add **Sn** on platinum foil. A black precipitate indicates **Sb°**. (*2*) Add iron wire, obtaining **Sb°** and **Sn″**; filter and test the filtrate for **Sn** by $HgCl_2$ (Pieszczek, *Arch. Pharm.*, 1891, **229**, 667).

6. The sulphides of **As**, **Sb** and **Sn** are all decomposed by concentrated nitric acid, which furnishes a basis of an excellent separation of the arsenic from the antimony and tin (Vaughan, *American Chemist*, 1875, **6**, 41). The sulphides reprecipitated from the $(NH_4)_2S_X$ solution by HCl are well washed, transferred to an evaporating dish, heated with concentrated HNO_3 until brown fumes are no longer evolved, and then evaporated to dryness, using sufficient heat to expel the HNO_3 and the H_2SO_4 formed by the action of the HNO_3 upon the **S**. The heating should be done on the sand bath. The cooled residue is digested for a few minutes with hot water, the arsenic passing into solution as H_3AsO_4, and the antimony and tin remaining as residue of Sb_2O_5 and SnO_2. The presence of arsenic may be confirmed by the reactions with $AgNO_3$ (§69, 6*j*), $CuSO_4$ (§69, 6*k*) by the Marsh test (§69, 6′*a*), or by precipitation with magnesia mixture (§69, 6*i*). A portion of the residue may be tested in the Marsh apparatus for the **Sb** (§70, 6*j*), another portion may be reduced and dissolved in an open dish with **Zn** and HCl (not allowable if **As** be present, §71, 10), and the resulting $SnCl_2$ identified by the reaction with $HgCl_2$ (§71, 6*i*).

7. The precipitated sulphides must be thoroughly washed to insure the removal of the ammonium salts, since in their presence the dangerously explosive nitrogen chloride (§268, 1) could be formed when the sulphides were dissolved in HCl with the aid of $KClO_3$.

8. Instead of chlorine ($HCl + KClO_3$), nitrohydrochloric acid may be employed, but it is liable to cause the formation of a white precipitate of Sb_2O_5 and SnO_2.

9. The chlorine should all be removed, as the metals cannot be reduced by the **Zn** and H_2SO_4 in the Marsh apparatus in the presence of powerful oxidizing agents as **Cl**. This would also require evaporation to expel the HNO_3, if nitrohydrochloric acid were used to effect solution.

10. Hydrogen peroxide, H_2O_2, decomposes the sulphides of arsenic and antimony with oxidation. The arsenic will appear in the solution, the antimony remaining as a white precipitate of the oxide (a sharp separation) (Luzzato, *Arch. Pharm.*, 1886, **224**, 772).

§87. **Manipulation.**—The solution of the metals of the tin group is then ready to be transferred to the Marsh apparatus (the directions for the use of the Marsh apparatus are given under arsenic (§69, 6′*a*), and should be carefully studied and observed. They will not be repeated here). Only a portion of the solution should be used in the Marsh apparatus, the remainder being reserved for other tests. The gas evolved from the Marsh apparatus is passed into a solution of silver nitrate, which by its oxidizing action effects a good separation between the arsenic and antimony (§89, 2):

$$AsH_3 + 6AgNO_3 + 3H_2O = H_3AsO_3 + 6Ag + 6HNO_3$$
$$SbH_3 + 3AgNO_3 = SbAg_3 + 3HNO_3$$

The hard glass tube of the Marsh apparatus is heated while the gas is being generated, a mirror of arsenic and antimony being deposited, due to the decomposition of the gases (§69, 6′*c*): $2SbH_3 = 2Sb + 3H_2$. The ignited gas is brought in contact with a cold porcelain surface for the production of the arsenic and antimony spots (§69, 6′*b*). Failure to obtain mirror, spots, or a black precipitate in the $AgNO_3$ is proof of the absence of both arsenic and antimony. The black precipitate obtained in the silver nitrate solution is separated by filtration, washed and reserved to be tested for antimony. The filtrate is treated with **HCl**, or a metallic chloride, as $CaCl_2$ or **NaCl**, to remove the excess of silver and, after evaporation to a small volume, is precipitated with H_2S. A lemon-yellow precipitate indicates arsenic. The black precipitate from the silver nitrate solution is dissolved in hot reagent **HCl**: $SbAg_3 + 6HCl = SbCl_3 + 3AgCl$. The excess of acid is removed by evaporation, a little water is added (§70, 5*d* and §59, 5*c*) and the **AgCl** removed by filtration. The filtrate is divided into two portions. To one portion H_2S is added; an orange precipitate indicates antimony. The H_2S may give a black precipitate of Ag_2S from the **AgCl** held in solution by the **HCl**. If this be the case, to the other portion one or two drops of **KI** are added and the solution filtered. This filtrate is now tested for the orange precipitate with H_2S.

The mirror obtained in the hard glass tube should be examined as directed in the text, especially by oxidation and microscopic examination (§69, 6′*c* 5). The spots should be tested with **NaClO** and by the other tests as given in the text (§69, 6′*c* 1).

§88. *Notes.*—**Arsenic.**—*1.* All compounds of arsenic are reduced to arsine by the **Zn** and H_2SO_4 in the Marsh apparatus. Hence if strong oxidizing agents are absent, the original solution or powder may be used directly in the Marsh apparatus for the detection of arsenic; but sulphides should not be present.

2. The burning arsine forms As_2O_3, which may be collected as a heavy white powder on a piece of black paper placed under the flame. Antimony will also deposit a similar heavy white powder.

3. The arsine evolved is not decomposed (faint traces decomposed) upon passing through a drying tube containing soda lime or through a solution of **KOH** (distinction and separation from antimony).

4. Arsenites and arsenates are distinguished from each other by the following reactions: (*a*) Arsenous acid solution acidulated with **HCl** is precipitated in the cold instantly by H_2S; arsenic acid under similar conditions is precipitated exceedingly slowly (§69, 6*c*). (*b*) Neutral solutions of arsenites give a yellow precipitate with $AgNO_3$; neutral solutions of arsenates give a brick-red precipitate. Both precipitates are soluble in acids or in ammonium hydroxide (§59, 6*g*). (*c*) Magnesia mixture precipitates arsenic acid as white magnesium ammonium arsenate, $MgNH_4AsO_4$; no precipitate with arsenous acid (§189, 6*g*). (*d*) **HI** gives free iodine with arsenic acid; not with arsenous acid (§69, 6*f*). (*e*) Alkaline solutions of arsenous acid are immediately oxidized to the pentad arsenic compounds by iodine (§69, 10). (*f*) Potassium permanganate is immediately decolored by solutions of arsenous acid or arsenites; no reaction with arsenates (§69, 10).

§89. *Notes.*—**Antimony.**—*1.* If antimony be present in considerable amount, it (in the form of the sulphide) is most readily separated from arsenic by boiling with strong **HCl** (solution of the antimony sulphide, (§70, 6*e*)); or by digesting with $(NH_4)_2CO_3$ or NH_4OH (solution of the arsenic (§69, 5*c*)).

2. For the detection of traces of antimony, the most certain test is in its volatilization as stibine in the Marsh apparatus and precipitation as $SbAg_3$, antimony argentide, with $AgNO_3$; this is a good separation from arsenic and tin, and after filtration it remains to dissolve the $SbAg_3$ in concentrated **HCl** and identify the **Sb** as the orange precipitate of Sb_2S_3. The formation of the black precipitate in the $AgNO_3$ solution must not be taken as evidence of the presence of antimony, as arsine gives a black precipitate of metallic silver with $AgNO_3$. A trace of antimony may be found in the filtrate from the $SbAg_3$, hence a slight yellow-orange precipitate from this solution must not be taken as evidence of arsenic without further examination (§69, 7).

3. Sb_2S_3 is precipitated from solutions quite strongly acid with **HCl**, *i. e.*, in the presence of equal parts of the concentrated acid (*sp. gr.* 1.20). Tin is not precipitated as sulphide if there be present more than one part of the concentrated acid to three of the solution (§70, 6*e*). This is a convenient method of separation. The addition of one volume of concentrated **HCl** to two volumes of the solution under examination before passing in the H_2S will prevent the precipitation of the tin while allowing the complete precipitation of the antimony.

4. If the sulphides of **As**, **Sb** and **Sn** are evaporated to dryness with concentrated HNO_3; the residue strongly fused with Na_2CO_3 and **NaOH**; and the cooled mass disintegrated with cold water, the filtrate will contain the arsenic as sodium arsenate, Na_3AsO_4, and the tin as sodium stannate, Na_2SnO_3; while the antimony remains as a residue of sodium pyroantimonate, $Na_2H_2Sb_2O_7$ (§70, 7).

5. Stibine is evolved much more slowly than arsine in the Marsh apparatus, and some metallic antimony will nearly always be found in the flask with the tin (§70, 6*j*).

6. If organic acids, as tartaric or citric, be present, they should be removed by careful ignition with K_2CO_3 as preliminary to the preparation of the substance for analysis, since they hinder the complete precipitation of the antimony with H_2S (§70, 6*e*).

7. Antimonic compounds are reduced to the antimonous condition by **HI** with liberation of iodine (§70, 6*f* and 10). Chromates oxidize antimonous salts to antimonic salts with formation of green chromic salts (§70, 6*h*). $KMnO_4$ also oxidizes antimonous salts to antimonic salts, a manganous salt being formed in acid solution (§70, 6*h*). No reaction with antimonic salts. Antimonous salts reduce gold chloride; antimonic salts do not (§73, 10).

§90. **Manipulation.**—The contents of the generator of the Marsh apparatus should be filtered and washed. The filtrate, if colorless, may be

rejected (absence of **Mo**). A colored filtrate, blue to green-brown or black, indicates the probable presence of some of the lower forms of molybdenum. The solution should be evaporated to dryness with an excess of HNO_3, which oxidizes the molybdenum to molybdic acid, MoO_3. The residue is dissolved in NH_4OH (the zinc salt present does not interfere) and poured into moderately concentrated nitric or hydrochloric acid (§75, 6*d* footnote). This solution is tested for molybdenum by Na_2HPO_4. The original solution should also be examined for the presence of molybdenum as molybdic acid or molybdate (§75, 6*d*).

The residue from the generator of the Marsh apparatus may contain **Sb**, **Sn**, **Au**, and **Pt** with an excess of **Zn**. It should be dissolved as much as possible in **HCl**. **Sb**, **Au**, and **Pt** are insoluble (§70, 5*a*). The **Sn** passes into solution as $SnCl_2$ and gives a gray or white precipitate with $HgCl_2$, depending on amount of the latter present (§71, 6*j*):

$$SnCl_2 + HgCl_2 = SnCl_4 + Hg$$
$$SnCl_2 + 2HgCl_2 = 2HgCl + SnCl_4$$

The presence of **Sn″** should always be confirmed by its action in fixed alkali solution upon an ammoniacal solution of $AgNO_3$, giving **Ag°** (§71, 6*i*).

Au and **Pt** may be detected in the residue, but it is preferable to precipitate them from a portion of the original solution by boiling with ferrous sulphate (6*h*, §§73 and 74). Both metals are precipitated. They are then dissolved in nitro-hydrochloric acid and evaporated to dryness with ammonium chloride on the water bath. The residue is treated with alcohol which dissolves the double chloride of gold and ammonium, leaving the platinum double salt as a precipitate, which is changed to the metal upon ignition. The alcoholic solution is evaporated, taken up with water and the gold precipitated by treating with $FeSO_4$ (§73, 6*h*), by boiling with oxalic acid (§73, 6*b*), or by treating with a mixture of $SnCl_2$ and $SnCl_4$ (Cassius' purple) (§73, 6*g*).

If a portion of the original solution, free from HNO_3, be boiled with oxalic acid the gold is completely precipitated as the metal, separation from the platinum which is not precipitated (§74, 6*b*).

§91. —*Notes.*— **Molybdenum.** *1.* In the regular course of analysis, molybdenum remains in the flask of the Marsh apparatus as a dark colored solution, the **Zn** and H_2SO_4 acting as a reducing agent upon the molybdic acid.

2. If the molybdenum be present in solution as molybdic acid or a molybdate, it may be separated in the acid solution from the other metals by phosphoric acid in presence of ammonium salts, forming the ammonium phosphomolybdate; insoluble in acids, but soluble in ammonium hydroxide (§75, 6*d*).

3. In ammoniacal solution of a phosphomolybdate, magnesium salts precipitate the phosphoric acid, leaving the molybdenum as ammonium molybdate in solution, which may be evaporated to crystallization (method of recovering ammonium molybdate from the ammonium phosphomolybdate residues).

§92. **Tin.** *1.* Tin requires the presence of much less **HCl** to prevent its precipitation by H_2S than arsenic or antimony (§89, *3*).

2. The yellow ammonium sulphide $(NH_4)_2S_x$ must be used to effect solution if tin (Sn'') be present, **SnS** being practically insoluble in the normal ammonium sulphide (§71, 5*c*).

3. Tin in the stannous condition, dissolved in the fixed alkalis (stannites), readily precipitates metallic silver black from solutions of silver salts. An arsenite (hot) or an antimonite in solution of the fixed alkalis produces the same result, but not if the silver salt be dissolved in a great excess of ammonium hydroxide (§70, 6*i*). This reaction also detects stannous salts in the presence of stannic salts.

4. Tin in the Marsh apparatus is reduced to the metal, and then by solution of the residue in **HCl**, forms $SnCl_2$, which may be detected by the reduction of $HgCl_2$ to **HgCl** or **Hg**° (§71, 6*j*), and by the action in fixed alkali solution upon the strong ammoniacal solution of silver oxide (§71, 6*i*).

5. If the **Zn** in the Marsh apparatus is completely dissolved, the **Sn** must be looked for in the solution, which in this case must not be rejected. The tin remains as the metal as long as zinc is present (§135, 10).

6. The presence of the tin may be confirmed by its action as a powerful reducing agent (§71, 10). If it be present as Sn^{IV}, these tests must be made after reduction in the Marsh apparatus or in an open dish with zinc and **HCl**.

§93. **Gold.**—*1.* Gold will usually be met with in combination with other metals as alloys, and is separated from most other metals by its insolubility in all acids except nitrohydrochloric acid.

2. If more than 25 per cent of gold be present in an alloy, as with silver, the other metal is not removed by nitric acid (§73, 5*a*). Either nitrohydrochloric acid must be used or the alloy fused with about ten times its weight of silver or lead, and this alloy dissolved in nitric acid when the gold remains behind.

3. If the presence of gold is suspected in the solution, it should be precipitated with $FeSO_4$ before proceeding with the usual method of analysis.

4. If gold be present (in the usual method of analysis) it will remain as a metallic residue in the Marsh apparatus, insoluble in **HCl** and may be identified by the reactions for **Au**°.

5. The reactions of gold chloride with the chlorides of tin forming Cassius' purple (§73, 6*g*) is one of the most characteristic tests for gold.

§94. **Platinum.**—*1.* Notes *1* to *4* under gold apply equally well for platinum, except that it is necessary to *boil* with $FeSO_4$ to insure complete precipitation of the platinum.

2. Oxalic acid is the best reagent for the separation of gold from platinum (§73, 6*b*).

3. The most important problems in the analysis of platinum consist in its separation from the other metals of the platinum ores (§74, 3).

§96. **Manipulation.**—The well washed residue after digesting the precipitated sulphides of the second group (the Tin and Copper Group) in $(NH_4)_2S_x$ may contain any of the metals of the Copper Group, and in addition frequently contains sulphur, formed by the action of the H_2S upon oxidizing agents: $4FeCl_3 + 2H_2S = 4FeCl_2 + 4HCl + S_2$. Pierce the point of the filter with a small stirring rod and, with as little water as possible, wash the precipitate into a test-tube, beaker, or small casserole. Sufficient reagent nitric acid (§324) should be added to make about one part of the acid to two parts of water and the mixture boiled vigorously for two or three minutes: *

$$2Bi_2S_3 + 16HNO_3 = 4Bi(NO_3)_3 + 4NO + 8H_2O + 3S_2$$
$$6CdS + 16HNO_3 = 6Cd(NO_3)_2 + 4NO + 8H_2O + 3S_2$$

* If preferred the precipitate on the filter may be washed with the boiling hot nitric acid of the above mentioned strength, pouring the same acid back upon the precipitate, reheating each time, until no further action takes place.

§95. Table for Analysis of the Copper Group (Second Group, Division A).

Sulphides not Soluble in Yellow Ammonium Sulphide: HgS, PbS, Bi_2S_3, CuS, CdS.*

If tin group sulphides (§84) have been found, the precipitate should be washed, first with $(NH_4)_2S_x$ (or Na_2S), then with hot water. Digest the precipitate with hot, moderately dilute **nitric acid.** Filter.

Residue:

HgS, (S, $PbSO_4$).

Dissolve the black precipitate in **nitrohydrochloric acid,** or in $HCl + KClO_3$, and expel the free chlorine by boiling.

Test the solution for **Hg''** with **stannous chloride** (§58, 6*g*); with **ammonium hydroxide** (§58, 6*a*); and with metallic **copper** (§58, 10).

Solution: $Pb(NO_3)_2$, $Bi(NO_3)_3$, $Cu(NO_3)_2$, $Cd(NO_3)_2$, HNO_3.

Add about three cc. of H_2SO_4,† concentrated, to the solution and evaporate over the naked flame or on the sand bath, until fumes of SO_3 are given off. This expels the HNO_3, which is detrimental to a complete precipitation of $PbSO_4$ (§57, 5*c*). Cool and dilute with about 15 cc. of water.

Precipitate:

$PbSO_4$.†

Wash and dissolve in warm ammonium acetate solution, add K_2CrO_4 solution and heat (§57, 6*h*). (Lead chromate is soluble in potassium hydroxide and is reprecipitated with acetic acid.)

To a portion of the precipitate of $PbSO_4$ add two drops of a one per cent solution of **KI**, giving yellow PbI_2 (§57, 6*f*).

Filtrate: $Bi_2(SO_4)_3$, $CuSO_4$, $CdSO_4$, (H_2SO_4).

Add **ammonium hydroxide** to a distinctly alkaline reaction. Warm, filter and wash.

Precipitate:

$Bi(OH)_3$.

A portion of the white precipitate should be removed, dissolved in **HCl** (the excess of acid removed by evaporation), and a portion tested for bismuth by pouring into water. A white precipitate indicates bismuth (§76, 5*d*). (Antimony would give the same results, but if the previous directions have been followed, it cannot be present, §70, 6*e*). To another portion of the **HCl** solution add **KI** drop by drop. A

Filtrate: Solutions of **copper** and **cadmium** sulphates in **ammonium hydroxide.**

The solution will be of a deep blue color if more than traces of copper are present. Add **KCN** to the blue solution until the blue color disappears and then add H_2S or $(NH_4)_2S$.

Precipitate:

CdS, yellow.

Solution:

$K_3Cu(CN)_4$, not precipitated by sulphides (§77, 6*b* and *e*).

If the solution, after adding **NH_4OH,** be nearly colorless, it may contain traces of copper, which may be

		black precipitate dissolving to a yellow solution indicates bismuth, §76, 6*f*. Another portion of the white precipitate should be treated with a hot solution of potassium stannite or formaldehyde (§71, 6*a*). A black precipitate is proof of the presence of bismuth (§76, 6*g*).		detected by acidifying with acetic acid and adding $K_4Fe(CN)_6$. A brown precipitate indicates copper; $Cd_2Fe(CN)_6$ is white (§77, 6*b*). If the blue solution be made acid with acetic acid, a clean iron wire will give a bright coating of metallic copper (§77, 10).
Follow the text at §58, 6; §80, §81 §96 and §97.	Follow the text at §57, 6; §80, §81, §96, §97, §98 and §99.	Follow the text at §76, 6; §80, §81, §96, §100, §101.	Follow the text at §78, 6; §80, §81, §96, §100, §102, §103.	Follow the text at §77, 6; §80, §81, §96, §99, *5*; §100, §102, §103.

* If silver was not removed by **HCl**, it may be detected in the nitric acid solution of this precipitate.

† If lead has been found in the **silver group**, it will inevitably be present in the copper group and must be removed. If it was *not* found in the **silver group** it still may be present in the copper group (§57, 6*f*). A portion of the above solution may be tested for lead with sulphuric acid and alcohol and if none be present, this step may be omitted with the remainder of the solution.

Mercuric sulphide is unattacked (§58, 6*e*) and remains as a black precipitate together with some sulphur as a yellow to brown-black precipitate. The precipitate is filtered and washed with a small amount of hot water. The filtrate is set aside to be tested later, and the black residue on the filter is dissolved in nitro-hydrochloric acid: $2HgS + 2Cl_2 = 2HgCl_2 + S_2$. This solution is boiled to expel all chlorine and the presence of mercury determined by reduction to **HgCl** or **Hg°** by means of $SnCl_2$ (§58, 6*g*): $HgCl_2 + SnCl_2 = Hg + SnCl_4$, $2HgCl_2 + SnCl_2 = 2HgCl + SnCl_4$; or by the deposition of a mercury film on a strip of bright copper wire (§58, 10): $HgCl_2 + Cu = Hg + CuCl_2$. Confirm further by bringing in contact with iodine in a covered dish: $Hg + I_2 = HgI_2$ (Jannaesch, *Z. anorg.*, 1896, **12**, 143). The mercury may also be detected by using NH_4OH and **KI** as the reverse of the Nessler's test (§207, 6*k*) (delicate 1 to 31,000) (Klein, *Arch. Pharm.*, 1889, **227**, 73).

§97. *Notes.—1.* The concentration of HNO_3 (1-2) is necessary for the solution of the sulphides of **Pb**, **Bi**, **Cu** and **Cd**, and may also dissolve traces of **HgS**. However, the concentrated HNO_3 (*sp. gr.*, 1.42) dissolves scarcely more than traces of **HgS** (§58, 6*e*). Long-continued boiling of **HgS** with concentrated HNO_3 changes a portion of the **HgS** to $Hg(NO_3)_2.HgS$, a white precipitate, insoluble in HNO_3.

2. In the use of nitrohydrochloric acid to dissolve the **HgS**, the **HCl** should be used in excess to insure the decomposition of the nitric acid, which would interfere with the reduction tests with $SnCl_2$ and **Cu°**. One part of HNO_3 to three parts **HCl** gives about sufficient **HCl** to decompose all the HNO_3, hence in this reaction a little more than that proportion of **HCl** should be used.

3. A small amount of black residue left after boiling the sulphides with HNO_3 may consist entirely of sulphur, which can best be determined by burning the residue on a platinum foil and noting the appearance of the flame, the odor, and the disappearance of the residue. The residue of sulphur frequently possesses the property of elasticity (§256, 1).

4. Boiling the sulphides of the copper group with HNO_3 will always oxidize a trace at least of sulphur to H_2SO_4 (§256, 6*B*, *2*), which will form $PbSO_4$ if any lead be present:

$$S_2 + 4HNO_3 = 2H_2SO_4 + 4NO$$
$$3PbS + 8HNO_3 = 3PbSO_4 + 4H_2O + 8NO$$

If the boiling be not continued too persistently, the amount of $PbSO_4$ formed is soluble in the HNO_3 present (§57, 5*c*), and does not at all remain behind with the **HgS**.

5. Even if only 1 to 2 mg. of **As** or **Sb** are present with a large quantity (500 mg.) of an element of the copper group enough is dissolved by either $(NH_4)_2S$ or $(NH_4)_2S_x$ for the detection of these metals. If only 3 to 5 mg. of **Sn** are present with a large quantity of elements of the copper group, all of the tin may remain undissolved. When **Cd** is present and the tin is in the stannous state as much as 15 mg. of **Sn** may remain undissolved even in the polysulphide (A. A. Noyes, J. Am. Chem. Soc. **29**, 170). The **Sn** or **Sb** (present on account of an insufficiency of $(NH_4)_2S_x$) will appear as a white precipitate mixed with the black precipitate of **HgS**, due to the fact that HNO_3 decomposes the sulphides of **Sb** and **Sn**, forming the insoluble Sb_2O_5 and SnO_2:

$$6Sb_2S_3 + 20HNO_3 = 6Sb_2O_5 + 9S_2 + 20NO + 10H_2O$$

If these metals have not been detected this precipitate must be tested. After testing for mercury in a portion of the precipitate, the paper may be burned

in a porcelain crucible and the residue fused with sulphur and sodium carbonate in the covered crucible. The tin and antimony will be converted into soluble thio salts and tested for according to § 84.

6. Traces of mercury may be detected by using a tin-gold voltaic couple. The Hg deposits on the Au, and can be sublimed and identified with iodine vapor. Arsenic gives similar results (Lefort, *C. r.*, 1880, **90**, 141).

7. Mercury may quickly be detected from all of its compounds by ignition in a hard glass tube with fusion mixture ($Na_2CO_3 + K_2CO_3$) (§58, 7), and then adding a few drops of HNO_3 (concentrated) and a small crystal of KI. Upon warming the iodine sublimes and combines with the sublimate of Hg, forming the scarlet red HgI_2. As and Sb both give colored compounds with iodine, decomposed by HNO_3 (Johnstone, *C. N.*, 1889, **59**, 221).

§98. **Manipulation.**—To the filtrate containing the nitric acid solution of the sulphides of Pb, Bi, Cu, and Cd, should be added about two cc. of concentrated H_2SO_4 and the mixture evaporated on a sand bath or over the naked flame in a casserole or evaporating dish until the fumes of H_2SO_4 are given off:

$$Pb(NO_3)_2 + H_2SO_4 = PbSO_4 + 2HNO_3$$
$$Cu(NO_3)_2 + H_2SO_4 = CuSO_4 + 2HNO_3$$

About 20 cc. of 50 per cent alcohol should be added to the well cooled mixture and the whole transferred to a small glass beaker. Upon giving the beaker a rotatory motion the heavy precipitate of $PbSO_4$ will collect in the center of the beaker, and its presence even in very small amounts may be observed. The filtrate from the $PbSO_4$ should be decanted through a wet filter, and the $PbSO_4$ in the beaker may be further identified by its transference into the yellow chromate with K_2CrO_4 or into the yellow iodide with KI (**57**, 6*f* and *h*).

§99. *Notes.—1.* In analysis, if lead was absent in the silver group, it is advantageous to test only a portion of the nitric acid solution with H_2SO_4 for lead, and if that metal be not present, the above step may be omitted with the remainder of the solution and the student may proceed at once to look for Bi, Cu and Cd. If, however, lead is present, the whole of the solution must be treated with H_2SO_4.

2. The nitric acid should be removed by the evaporation, as $PbSO_4$ is quite appreciably soluble in HNO_3 (§57, 5*c*).

3. The H_2SO_4 should be present in some excess, as $PbSO_4$ is less soluble in dilute H_2SO_4 than in pure water (§57, 5*c*).

4. Alcohol should be present, as it greatly decreases the solubility of $PbSO_4$ in water or in dilute H_2SO_4 (§57, 5*c*, 6*e*).

5. Too much alcohol must not be added, as sulphates of the other metals present are also less soluble in alcohol than in water (§77, 5*c*). These sulphates, if precipitated by the alcohol, are readily dissolved on dilution with water.

6. If the $(NH_4)_2S_X$ had not been well removed by washing, ammonium sulphate would be present at this point, greatly increasing the solubility of $PbSO_4$ (§57, 5*c*).

§100. **Manipulation.**—The filtrate from the $PbSO_4$ should be boiled to expel the alcohol (or if Pb be absent evaporate the nitric acid solution of division B) and then carefully neutralized with NH_4OH. An excess of

NH_4OH should be added to dissolve the precipitates of $Cu(OH)_2$ and $Cd(OH)_2$, leaving the $Bi(OH)_3$ as a white precipitate. The solution should be filtered, the precipitate thoroughly washed, and then treated upon the filter with a hot solution of potassium stannite, K_2SnO_2. A black precipitate is evidence of the presence of **Bi** (§76, 6*g*).

§101. *Notes.—1.* If the precipitate of the sulphides of the second group was not well washed, the hydroxides of the metals of the iron group (**Al**, **Cr** and **Fe**) may be present at this point. The precipitate of $Al(OH)_3$ would be white, but would not give a black precipitate with K_2SnO_2.

2. If an insufficient quantity of $(NH_4)_2S_X$ was used, **Sb** and **Sn** would be present and give a white precipitate with the NH_4OH.

3. If the lead had not been removed it would appear as a white precipitate with the NH_4OH, and would give a brownish-black precipitate with the hot K_2SnO_2 (§57, 6*g*). The presence of a permanent white precipitate with NH_4OH must never be taken as final evidence of the presence of **Bi**.

4. As a confirmatory test for the presence of **Bi**, a portion of the white precipitate with NH_4OH should be dissolved in **HCl** and the solution evaporated nearly to dryness to remove the excess of **HCl**. Now upon adding water, a white precipitate of **BiOCl**, bismuth oxychloride, will be obtained if **Bi** is present (§76, 5*d*).

§102. **Manipulation.**—If the ammoniacal filtrate from the $Bi(OH)_3$ is of a blue color, that is sufficient evidence of the presence of **Cu** unless nickel was precipitated in the second group. In absence of a blue color a portion of the solution should be acidulated with acetic acid and then to this solution a few drops of potassium ferrocyanide, $K_4Fe(CN)_6$, should be added. A brick-red precipitate is evidence of copper. Or to the acidulated solution a bright nail or piece of iron wire may be added, obtaining a film of metallic copper. If sufficient copper be present to give a blue color to the solution, before testing for cadmium a solution of **KCN** should be added until the blue color disappears. Then the addition of H_2S will give a yellow precipitate for cadmium.

§103. *Notes.—1.* The precipitate of the brick-red $Cu_2Fe(CN)_6$ is a much more delicate test for copper than the blue color to the ammoniacal solution (§77, 6*b*). **Cd** gives a white precipitate, insoluble in the acid.

2. The student should not forget that in the regular course of analysis a trace of copper may be lost by the solubility of the sulphide in $(NH_4)_2S_X$. If mercury has been shown to be absent, the sulphides of the tin group (second group, division A) should be dissolved by the addition of a fixed alkali sulphide (§71, 6*c*), K_2S or Na_2S, which does not dissolve **CuS**. In case mercury be present, the presence or absence of small amounts of copper must be determined by the usual reactions for copper upon the original solution, having due regard for the possible interference of metals which the analysis has shown to be present.

3. Potassium cyanide, **KCN**, in excess changes cupric salts to the soluble double salt of cuprous cyanide and potassium cyanide, $K_3Cu(CN)_4$, which is colorless and not precipitated by sulphides. With cadmium salts the soluble double cyanide, $K_2Cd(CN)_4$, is formed, which is decomposed by sulphides forming **CdS**, yellow.

4. If preferred, the sulphides of **Cu** and **Cd** may be precipitated from the ammoniacal solution by H_2S and then the black **CuS** dissolved with **KCN**, leaving a yellow precipitate of **CdS**.

5. Copper and cadmium may be separated from each other by reduction of the copper (from the ammoniacal solution acidulated with **HCl**) with $SnCl_2$ (§77, 10): $2CuCl_2 + SnCl_2 = 2CuCl + SnCl_4$, and its precipitation with milk of sulphur (§77, 6*c*), forming Cu_2S, removal of the tin with NH_4OH and the precipitation of the cadmium with H_2S.

6. From the solutions of copper and cadmium acidulated with **HCl**, a hot solution of $Na_2S_2O_3$ precipitates the copper as Cu_2S (§77, 6*c*), while the cadmium remains in solution. From this solution the cadmium is detected as the sulphide by neutralization with NH_4OH and precipitation with H_2S or $(NH_4)_2S$.

7. The ammoniacal solution of **Cu** and **Cd** may be precipitated with H_2S, and the resulting sulphides, after filtering and washing, boiled with hot dilute H_2SO_4 (one of acid to five of water). In this solution the **CuS** (§77, 5*c*) is unattacked while the **CdS** is dissolved. The filtrate upon dilution with water gives the yellow **CdS** with H_2S or $(NH_4)_2S$ (§78, 6*e*).

Rarer Metals of the Tin and Copper Group.

(*Second Group.*)

Ruthenium, Rhodium, Palladium, Iridium, Osmium, Tungsten, Germanium, Tellurium, Selenium.

§104. Ruthenium. Ru = 101.7. Valence two to eight.

1. Properties.—*Specific gravity*, 11.0 to 11.4 (Deville and Debray, *C. r.*, 1876, **83**, 926). Melting-point 2450°? (*Cir. B. S.*, **35**, 1915). Next to osmium it is the most difficultly fusible of all the platinum metals. A black powder or a grayish-white crystalline brittle metal.

2. Occurrence.—In small quantities in platinum ores.

3. Preparation.—Ignite the **Pt** residues in a stream of chlorine in presence of **NaCl**. Dissolve the fused mass in H_2O, add KNO_2, neutralize with Na_2CO_3, evaporate to dryness and extract the double nitrites with absolute alcohol (separation from rhodium). Add water to the solution, distill off the alcohol, add **HCl** and obtain a red solution of potassium ruthenium chloride. This is changed to the double ammonium salt and then precipitated with $HgCl_2$, which upon recrystallization and ignition gives pure **Ru** (Gibbs, *Am. S.*, 1862, (2), **34**, 349 and 355).

4. Oxides and **Hydroxides.**—The hydroxides, $Ru(OH)_2$, $Ru(OH)_3$, and $Ru(OH)_4$, are precipitated from the respective chlorides by **KOH**. They are dark brown to black. Perruthenic anhydride or acid, RuO_4, is a golden yellow crystalline powder, volatile even at ordinary temperatures. It has a peculiar odor, somewhat like ozone, is sparingly soluble in water, melts at 50° and boils at a little over 100° (Deville and Debray, *B.*, 1875, **8**, 339). It is prepared by heating K_2RuCl_5 with **KOH** into which a current of chlorine is passed or by distillation of a **Ru** salt with $KClO_3$ and **HCl**. The vapor is yellow and is strongly irritating to the membrane of the throat.

5. Solubilities.—**Ru** is soluble with difficulty in nitrohydrochloric acid, insoluble by fusion with $KHSO_4$, but is soluble by fusion with **KOH**, especially in presence of KNO_3. Soluble in chlorine, forming a mixture of $RuCl_2$, $RuCl_3$, and $RuCl_4$. The double nitrites are soluble in water and alcohol (separation from rhodium).

6. Reactions.—The alkalis precipitate from ruthenic chloride the dark yellow hydroxide, soluble in acids, insoluble in the fixed alkalis, soluble in NH_4OH with a greenish-brown color. H_2S precipitates slowly the black sulphide (formed at once by $(NH_4)_2S$), the solution becoming blue. The sulphide is **insoluble** in alkali sulphides. **KI** gives with hot solutions a black precipitate

of ruthenic iodide. **KCNS** forms, after some time in the cold, a red coloration, which upon heating assumes a beautiful violet color (characteristic). The double nitrites are soluble, and if to the solution $(NH_4)_2S$ be added, a characetristic crimson red liquid is obtained. Upon standing the solution becomes brown, or a brown precipitate is caused by excess of the $(NH_4)_2S$.

7. **Ignition.**—If RuO_4 be heated to a dull-red heat the violet-blue dioxide is formed (Debray and Joly, *C. r.*, 1888, **106**, 328).

8. **Detection.**—By oxidation and distillation as RuO_4.

9. **Estimation.**—Reduced to the metal and weighed as such.

10. **Oxidation.**—RuO_4 heated with **HCl** forms $RuCl_3$, evolving chlorine. Ru^{8-x} is changed to RuO_4 by distilling with $KClO_3$ and **HCl**. **Zn** reduces **Ru** solutions to the metal, with an indigo-blue color during transition from Ru^{IV} to Ru^{II}.

§105. Rhodium. Rh = 102.9. Valence two, three and four.

1. **Properties.**—*Specific gravity*, 12.1 (Deville and Debray, *C. r.*, 1874, **78**, 1782). *Melting point*, 1950° (*Cir. B. S.*, **35**, 1915). It is a white metal, nearly as ductile and malleable as Ag. The metal precipitated by alcohol or formic acid appears as a black spongy mass (Wilm, *B.*, 1881, **14**, 629).

2. **Occurrence.**—Found in platinum ores.

3. **Preparation.**—Fusion of the **Pt** residues with **Pb**, digestion with HNO_3 and then **Cl**, converting the **Rh** into the chloride, from which solution it is precipitated as the double ammonium chloride by fractional precipitation. See Gibbs (*J. pr.*, 1865, **94**, 10) and Wilm (*B.*, 1883, **16**, 3033).

4. **Oxides** and **Hydroxides.**—$Rh(OH)_3$ is precipitated from a solution of sodium rhodium chloride by an excess of **KOH**. It is a black gelatinous precipitate, forming the oxide upon ignition. Rhodium fused with **KOH** and KNO_3 gives RhO_2, a brown powder, insoluble in acids or alkalis.

5. **Solubilities.**—The pure metal or the alloy with **Au** or **Ag** is almost insoluble in acids; alloyed with **Bi**, **Pb**, **Cu** or **Pt**, it is soluble in HNO_3 (Deville and Debray, *l. c.*). Attacked by chlorine the most easily of all the **Pt** metals. The precipitated metal, a gray powder, is soluble in **HCl** in presence of air to a cherry-red color.

6. **Reactions.**—**Alkali hydroxides** and **carbonates** precipitate solutions of **Rh** salts as $Rh(OH)_3$, yellow, insoluble in acids, soluble in excess of NH_4OH, forming a rhodium ammonium base, precipitated by **HCl** as a bright yellow crystalline salt, chloro-purpureo-rhodium chloride, $Rh(NH_3)_5Cl_3$. Alkali nitrites precipitate alcoholic solutions of rhodium chloride as alkali-rhodium nitrite (Gibbs, *Am. S.*, 1862, (2), **34**, 341) (separation from ruthenium). From a hot solution of **Rh** salt, H_2S precipitates the sulphide, insoluble in the alkali sulphides; the sulphide precipitated from the cold solution is soluble in alkali sulphides. **KI** precipitates from hot solutions a black-brown rhodium iodide.

7. **Ignition.**—When the metal or its compounds are repeatedly fused with HPO_3 or $KHSO_4$, the corresponding **Rh** salts are formed. The mass fused with $KHSO_4$ is soluble in water to a yellow color, turning red with **HCl**.

8. **Detection.**—By ignition as given above. Also to the concentrated neutral solution add fresh **NaClO** solution. To the yellow precipitate add a small amount of $HC_2H_3O_2$ and shake till an orange-yellow solution is obtained. After a short time the solution becomes colorless, then a gray precipitate separates out and the solution assumes a sky-blue color (Demarcay, *C. r.*, 1885, **101**, 951).

9. **Estimation.**—It is reduced to the metal and weighed as such.

10. **Oxidation.**—Solutions of rhodium salts are reduced to the metal by **Zn**. All **Rh** compounds are reduced to the metal by heating in a current of hydrogen.

10. **Oxidation.**—Solutions of rhodium salts are reduced to the metal by **Zn**. All **Rh** compounds are reduced to the metal by heating in a current of hydrogen.

§106. Palladium. Pd = 106.7. Valence two and four.

1. **Properties.**—*Specific gravity*, 11.4 (Deville and Debray, *C. r.*, 1857, **44**, 1101). *Melting point* 1549° (*Cir. B. S.*, **35**, 1915). It conducts electricity about one-eighth as well as silver (Matthiessen, *Pogg.*, 1858, **103**, 428). Palladium has about the color and lustre of silver. The metal when only slightly heated assumes a rainbow tint from green to violet. Because of its general properties, it is to be classed with the platinum metals, yet in its reaction with acids it is markedly different. In the air at ordinary temperature it is but slightly tarnished, but at a red heat it becomes covered with a coating of the oxide. The finely divided metal, *palladium sponge*, absorbs many times its volume of hydrogen, retaining the most of the hydrogen even at 100°. At a high heat the hydrogen is all driven off. It is much used in gas analysis for the separation of hydrogen from other gases (Hempel, *B.*, 1879, **12**, 636, 1006). Also used for scale graduations of the best scientific instruments.

2. **Occurrence.**—It is a never-failing element in the platinum ores, native or alloyed with **Pt**, **Au** or **Ag**.

3. **Preparation.**—The obtaining of pure palladium involves its separation from the other platinum metals, *i. e.*, platinum, iridium, osmium, rhodium and ruthenium. The student is referred to the various works on metallurgy; also to the following: Bunsen, *A.*, 1868, **146**, 265; Wilm, *B.*, 1885, **18**, 2536; and Mylius and Forster, *B.*, 1892, **25**, 665.

4. **Oxides** and **Hydroxides.**—Palladium monoxide, **PdO**, is the most stable of the oxides of **Pd**. It is formed by the gentle ignition of $Pd(NO_3)_2$ or the precipitation of $PdCl_2$ with Na_2CO_3, forming $Pd(OH)_2$, and then igniting. Palladic oxide, PdO_2, when gently ignited loses half its oxygen, becoming **PdO**.

5. **Solubilities.**—*a.—Metal.*—It is slowly dissolved by boiling with **HCl** or H_2SO_4; HNO_3 dissolves it, even in the cold, forming $Pd(NO_3)_2$. It is more readily soluble in nitrohydrochloric acid, forming $PdCl_4$. It is not at all attacked by H_2S. An alcoholic solution of iodine blackens it, and when fused with $KHSO_4$ it becomes the sulphate (distinction from platinum). *b.—Oxides.*—PdO_2 is soluble in **HCl** with evolution of **Cl**, forming $PdCl_2$. $Pd(OH)_2$ is readily soluble in acids forming palladous salts. *c.—Salts.*—Palladic chloride, $PdCl_4$, the most stable of the palladic salts is decomposed by boiling with water or by much dilution with cold water, forming $PdCl_2$. It forms double chlorides with other metals, as calcium palladic chloride, $CaPdCl_6$, which for the most part are stable, and soluble in water and alcohol. Potassium palladic chloride, K_2PdCl_6, is but sparingly soluble in water, insoluble in alcohol; partially decomposed by both solvents.

Palladous *chloride* is readily soluble in water with a brownish-red color; with metallic chlorides, it forms double chlorides, as potassium-palladous chloride, K_2PdCl_4, all of which are soluble in water.—Palladous *iodide* is insoluble in water, alcohol or ether; insoluble in dilute hydrochloric acid or hydriodic acid; slightly soluble by iodides and by chlorides.—Palladous *nitrate*, $Pd(NO_3)_2$, is soluble in water with free nitric acid; the solution being decomposed by dilution, evaporation, or by standing, with precipitation of variable basic nitrates.—Palladous sulphate, $PdSO_4$, dissolves in water, but decomposes in solution on standing.

6. **Reactions.**—**Palladous chloride** is precipitated by **potassium hydroxide** or **sodium hydroxide**; as brown basic salt or as brown *palladous hydroxide*, $Pd(OH)_2$, soluble in excess of the hot reagents. **Ammonium hydroxide** gives a flesh-red precipitate of *palladio-diammonium chloride*, $(NH_3)_2PdCl_2$. The flesh-red precipitate is soluble in excess of the ammonia, and from this solution reprecipitated by hydrochloric acid, with a yellow color. The fixed alkali **carbonates** precipitate the hydroxide; ammonium carbonate acts like the hydroxide.—Potassium **cyanide** precipitates *palladous cyanide*, $Pd(CN)_2$, white, soluble in excess of the reagent. **Phosphates** give a brown precipitate.—**Hydrosulphuric acid** and sulphides precipitate the dark-brown *palladous sulphide*, **PdS**, **insoluble in the ammonium sulphides**, soluble in nitrohydrochloric acid. Potassium **iodide** precipitates *palladous iodide*, PdI_2, black, visible in 500,000 parts of the solution, with the slight solubilities stated in 5*c*, an important separation of iodine from bromine. In very dilute solutions, only a

color is produced, or the precipitate separates after warming. At a red heat, the precipitate is decomposed.

Palladous nitrate gives most of the above reactions; no precipitate with ammonia, and a less complete precipitate with iodides.

7. **Ignition.**—Nearly all the palladium compounds are reduced by heat, before the blow-pipe, to a "sponge." If this be held in the inner flame of an alcohol lamp, it absorbs carbon at a heat below redness; if then removed from the flame, it glows vividly in the air, till the carbon is all burnt away (distinction from platinum).

8. **Detection.**—Palladium is precipitated with the second group metals by H_2S, not dissolved by $(NH_4)_2S_x$ (separation from the tin group). It is distinguished from mercury by its precipitation as a cyanide with mercuric cyanide. It is precipitated from quite dilute solutions by **KI** (distinction from **Bi** and **Cd**); an excess of the **KI** dissolves the black palladous iodide, PdI_2, to a dark brown solution. **KCNS** does not precipitate palladium salts, not even after the addition of SO_2 (separation from **Cu**). The addition of H_2SO_4 and alcohol separates lead from palladium. The presence of the metal should be further confirmed by reduction and study of the properties of the "sponge" obtained.

9. **Estimation.**—(*1*) As metallic palladium, to which state it is reduced by mercuric cyanide or potassium formate, and ignition, first in the air and then in hydrogen gas. (2) As K_2PdCl_6. Evaporate the solution of palladic chloride with potassium chloride and nitric acid to dryness, and treat the mass when cold with alcohol, in which the double salt is insoluble. Collect on a weighed filter, dry at 100°, and weigh.

10. **Oxidation.**—Palladium is reduced as a dark-colored precipitate, from all compounds in solution, by sulphurous acid, stannous chloride, phosphorus, and all the metals which precipitate silver (§59, 10). Ferrous sulphate reduces palladium from its nitrate, not from its chloride. Alcohol, at boiling heat, reduces it; oxalic acid does not (distinction from gold §73, 6*b*).

§107. Iridium. Ir = 193.1. Usual valence three and four.

1. **Properties.**—*Specific gravity*, 22.421 (Deville and Debray, *C. r.*, 1875, **81**, 839). *Melting point* 2350° ? (*Cir. B. S.*, **35**, 1915). When reduced by hydrogen it is a gray powder, which by pressing and igniting at a white heat changes to a metallic mass capable of taking a polish. It is used mostly as an alloy with platinum, forming a very hard, durable material for standard weights and measures. A platinum-iridium dish containing 25 to 30 per cent iridium is not attacked by nitrohydrochloric acid.

2. **Occurrence.**—Found in platinum ores, usually as an alloy with platinum or osmium.

3. **Preparation.**—The platinum residues are mixed with **Pb** and **PbO** and heated at a red heat for one-half hour, then treated with acids. The residue contains the iridium as osmium-iridium or platinum-iridium with other platinum metals. This residue is mixed with **NaCl** in a glass tube and heated to a red heat in a current of chlorine. Much of the osmium passes over as the volatile perosmic acid, and is condensed. The double sodium chlorides of **Ir**, **Os**, **Rh**, **Pt**, **Pd** and **Ru** are dissolved in water, filtered and, when boiling hot, decomposed by H_2S. The iridium is reduced from the tetrad to the triad, but is not precipitated until after all the other metals. By stopping the current of H_2S just as the brown iridium sulphide begins to form, a complete separation can be made by filtration. By recrystallization the pure sodium double salt, $6NaCl.2IrCl_3 + 24H_2O$, is obtained, which is changed to the tetrad ammonium double salt, $(NH_4)_2IrCl_6$, by the addition of NH_4Cl and oxidation with chlorine (Wöhler, *Pogg.*, 1834, **31**, 161). This upon ignition gives the pure metal as iridium sponge. Or, the double sodium salt is ignited with sodium carbonate, exhausted with water and reduced by ignition in a current of hydrogen, leaving the metal as a fine gray powder. (See also §106, 3).

4. **Oxides** and **Hydroxides.**—Iridium forms two series of oxides and hydroxides, the metal acting as a triad and tetrad respectively. IrO_2 is formed by

igniting the metal in the air at a bright red heat, hence the *scaling of platinum dishes which contain iridium*. The hydroxide, $Ir(OH)_4$, is formed by boiling a solution of the trichloride, $IrCl_3$, in a fixed alkali hydroxide or carbonate. Careful addition of **KOH** to $IrCl_3$ in a vessel full of liquid and closed to exclude air gives $Ir(OH)_3$, easily oxidized to $Ir(OH)_4$ (Claus, *J. pr.*, 1846, **39**, 104).

5. **Solubilities.**—Freshly precipitated iridium may be dissolved in nitrohydrochloric acid. The ignited metal is insoluble in all acids. Its proper solvent is chlorine. Iridium trichloride, $IrCl_3$, is soluble in water and forms with the alkali chlorides double chlorides, soluble in water, insoluble in alcohol. The tetrachloride with sodium chloride, Na_2IrCl_6, is formed when the platinum residues mixed with **NaCl** are heated in a current of chlorine. It is soluble in water. The corresponding ammonium salt may be formed from the sodium salt by precipitation from the concentrated solution with NH_4Cl, a reddish-brown precipitate, soluble in 20 parts of water (Vauquelin, *A. Ch.*, 1806, **59**, 150 and 225). The potassium double salt is sparingly soluble in water.

6. **Reactions.**—**Fixed alkali hydroxides** or **carbonates** precipitate from boiling solutions of iridium chloride, $IrCl_3$ or $IrCl_4$, *iridium hydroxide*, $Ir(OH)_4$, dark blue, insoluble in all acids except **HCl**. Potassium nitrite added to a hot solution of iridium salts gives, first a yellow color and finally a yellow precipitate, insoluble in water or acids. **Hydrogen sulphide** reduces $IrCl_4$ to $IrCl_3$, and then precipitates the trisulphide, Ir_2S_3, brown, soluble in alkali sulphides.

7. **Ignition.**—When iridium is fused with potassium acid sulphate it is oxidized, but does not go into solution (difference from rhodium, §105, 7). Ignition on charcoal reduces all iridium compounds to the metal. Fusion in the air with sodium hydroxide or with sodium nitrate causes oxidation of the metal, the iridium oxide formed being partially soluble in the fixed alkali.

8. **Detection.**—See 3 and 6.

9. **Estimation.**—It is converted into the oxide by igniting with KNO_3 and then reduced by ignition in an atmosphere of hydrogen.

10. **Oxidation.**—Formic acid (from hot solution), zinc and H_2SO_4 or **HCl** reduce iridium compounds to the metal. $SnCl_2$, $FeSO_4$ and $H_2C_2O_4$ reduce tetrad iridium to triad, but do not further reduce (separation from gold, §73, 6*g*, *h* and *b*).

§108. Osmium. Os = 190.9. Valence two to eight.

1. **Properties.**—*Specific gravity*, 22,477, the heaviest of all bodies (Deville and Debray, *C. r.*, 1876, **82**, 1076). Melting point 2700°? (*Cir. B. S.*, **35**, 1915). In the absence of air it may be heated above the vaporization point of **Pt** without melting or oxidizing. In presence of air, when heated a little above the melting point of **Zn**, it burns to the volatile poisonous perosmic acid, OsO_4. In compact form it is very hard, cutting glass, and possesses a metallic lustre, with a bluish color resembling **Zn**.

2. **Occurrence.**—Always present in the residues of the platinum ores, in combination with iridium.

3. **Preparation.**—The iridium osmium alloy or other **Os** containing material is finely divided and distilled in a current of chlorine or with nitrohydrochloric acid, the osmium passing into a receiver containing **KOH**. By repeated additions of HNO_3 and further distillation, the osmium may all be driven into the receiver. The distillate is treated with **HCl** and **Hg** and the amalgam ignited in a current of hydrogen (Berzelius, *Pogg.*, 1829, **15**, 208).

4. **Oxides.**—Osmium forms five different oxides, **OsO**, Os_2O_3, OsO_2, OsO_3, OsO_4. The first three are bases, the salts of which have been but little studied; OsO_3 forms salts with bases, and OsO_4 acts rather as an indifferent peroxide. Perosmic acid, OsO_4, exists as white glistening needles, melting under 100°, sparingly soluble in water, its solution having a very penetrating odor, resembling that of chlorine. The fumes of the acid are very poisonous, and cause inflammation of the eyes. H_2S is recommended as an antidote (Clauss, *A.*, 1847, **63**, 355).

5. **Solubilities.**—The metal in compact condition is not at all attacked by any acid. The precipitated metal is slowly dissolved by nitrohydrochloric or fum-

ing nitric acid. By heating the metal in a current of chlorine a mixture of $OsCl_2$ and $OsCl_4$ is formed. They are both unstable.

6. **Reactions.**—Perosmic acid, OsO_4, when boiled with alkalis, is reduced to osmates, as K_2OsO_4. A solution of perosmic acid decolors indigo, oxidizes alcohol to aldehyde, and liberates iodine from potassium iodide. In the presence of a strong mineral acid, H_2S precipitates osmium sulphide, OsS_4, brownish black (Claus, *J. pr.*, 1860, **79**, 28); insoluble in alkali hydroxides, carbonates or sulphides.

7. **Ignition.**—Osmium when heated on a piece of platinum foil gives an intensely luminous flame of short duration. By holding the foil in the reducing flame and then again in the oxidizing flame, the luminosity may be repeated. If a mixture of the metal or of the sulphide and potassium chloride be heated in a current of chlorine, a double salt of potassium osmic chloride is formed, sparingly soluble in cold water, more readily in hot water. Alcohol precipitates it from its solutions as a red crystalline powder.

8. **Detection.**—By the intensely luminous flame when ignited on a platinum foil; by oxidation and distillation as perosmic acid and identification by odor, action on indigo and on potassium iodide.

9. **Estimation.**—It is weighed as the metal (see 3).

10. **Oxidation.**—OsO_4 is reduced to OsO_2 by ferrous sulphate. Zn and many other metals in presence of strong acids precipitate the metal. The metal is also obtained from all osmium compounds by ignition in a current of hydrogen.

§109. Tungsten (Wolframium). W = 184. Valence two to six.

1. **Properties.**—*Specific gravity*, 18.71–18.74 (*Z. Anorg*, 1909, 1910). *Melting point*, 3000° (*Cir. B. S.*, **35**, 1915). A tin-white or steel-gray metal, brittle, harder than agate. That precipitated from acid solutions is a velvet-black powder. Non-magnetic. Stable in the air at ordinary temperature; burning at a high temperature, it decomposes steam at a red heat. Dry metallic tungsten powder, compressed into a bar in a hydraulic press, may, by repeated heatings and swaging or rolling, be converted into a ductile form, and drawn into wire (*Met. and Cham. Eng.*, **3**, XII, 1914).

2. **Occurrence.**—Tungsten does not occur in nature in large amounts, nor is it widely disseminated. The most common tungsten minerals are scheelite, ($CaWO_4$), and wolframite ($FeWO_4$ and $MnWO_4$, in variable proportions). It never occurs native.

3. **Preparation.**—By reduction of WO_3 in H at a red heat (Zettnow, *Pogg.*, 1860, **111**, 16); by ignition of WO_3 and Na under NaCl. Tungstic acid of commerce is prepared by igniting for several hours: 100 parts Na_2CO_3, ignited; 150 parts finely ground wolframite; and 15 parts $NaNO_3$. The cooled mass is exhausted with water and the filtrate poured into hot, moderately concentrated HCl (Franz, *J. pr.*, 1871, (2), **4**, 238).

4. **Oxides.**—WO_2 is obtained as a brown powder by decomposing WCl_4 with water (Roscoe, *l. c.*). WO_3 is a lemon-yellow, soft powder, insoluble in water or acids. It is formed by ignition of the metal, lower oxides or decomposable salts in the air. The blue tungsten oxides are compounds between WO_2 and WO_3.

5. **Solubilities.**—The metal is scarcely at all attacked by HCl or H_2SO_4, slowly by HNO_3 or nitrohydrochloric, slowly soluble in alkalis. The halogens combine directly upon heating. WO_2 is readily soluble on heating with HCl and H_2SO_4, to a red color. It is also soluble in KOH with red color, evolving hydrogen. Both the acid and alkaline solutions deposit the blue oxide on standing (von der Pfordten, *A.*, 1884, **222**, 158). WO_3 is insoluble in water or acids, not even soluble in hot concentrated H_2SO_4. Soluble in KOH, K_2CO_3 and NH_4OH. In an atmosphere of CO_2 it reacts with the chlorides of Ca, Mg, Co, Ni and Fe (not with those of Pb, Ag, K and Na), *e. g.*, $MCl_2 + 2WO_3 = MWO_4 + WO_2Cl_2$. Heated with chlorine, WO_2Cl_2 is formed, and also WCl_4, decomposed by water. S, H_2S or HgS form WS_3 on heating with WO_3. Soluble alkali tungstates are formed by fusion of the acid, WO_3, with the alkali metal carbonates, more slowly by boiling with the carbonates. Acids form, from solutions of the alkali tungstates, a white precipitate of the hydrated acid turning yellow on boiling, insoluble in excess of the acids (dis-

tinction from MoO_3), soluble in NH_4OH. Phosphoric acid changes tungstic acid to the metatungstic acid, which is soluble in water and not precipitated by other acids. Long boiling of the solution of metatungstic acid causes the precipitation of tungstic acid. Fusion of WO_3 with $KHSO_4$ gives a compound of potassium tungstate and tungstic acid, not readily soluble in water but very readily soluble in $(NH_4)_2CO_3$ (distinction from silica, §249, 5).

6. **Reactions.**—Solutions of salts of Ba, Ca, Pb, Ag and Hg produce white precipitates with solutions of alkali tungstates. H_2S precipitates WS_2 from acid solutions, the sulphide dissolving readily in $(NH_4)_2S$, forming a thiotungstate $(NH_4)_2WS_4$. The tungstates, like the molybdates, form complex compounds with phosphoric acid, *i. e.*, phosphomolybdates and phosphotungstates, which react very similarly with ammonium salts and with organic bases (§75, 6*d*). $K_4Fe(CN)_6$ gives with tungstates (in presence of acids) a deep brownish-red fluid, forming after some time a precipitate of the same color. Solution of tannic acid gives a brown color or precipitate.

7. **Ignition.**—With $NaPO_3$, WO_3 dissolves, on fusion, to a clear or yellowish bead in the oxidizing flame; in the reducing flame it has a blue color, changing to red on addition of $FeSO_4$. Heated on charcoal in presence of Na_2CO_3 with the blow-pipe, using the reducing flame, the metal is obtained.

8. **Detection.**—If a tungstate be fused with Na_2CO_3, the mass warmed with water and the water then absorbed with strips of filter paper, the tungsten may be detected by moistening the strip with HCl and warming, obtaining the yellow color of WO_3; and the blue color of a lower oxide by moistening with $SnCl_2$ and warming. $(NH_4)_2S$ does not color the paper, even after adding HCl, but on warming a blue or green color is obtained.

9. **Estimation.**—It is converted into WO_3 and weighed as such after ignition.

10. **Oxidation.**—WO_3 gives with $SnCl_2$, or Zn in presence of HCl or H_2SO_4, a beautiful blue color, due to the formation of oxides between WO_2 and WO_3, *blue oxides of tungsten* (delicate and characteristic).

§111 Germanium. Ge = 72.5. Valence two and four.

1. **Properties.**—*Specific gravity*, 5.469 at 20.4° (Winkler, *J. pr.*, 1886, (2), **34**, 177); *melting point*, 958° (*Cir. B. S.*, **35**, 1915). A gray-white crystalline metal. Fused under borax it gives a grayish-white regulus with a metallic lustre. It is stable in the air, volatilized at a high heat (Meyer, *B.*, 1887, **20**, 497), and is easily pulverized. It burns in oxygen to form germanic oxide, GeO_2.

2. **Occurrence.**—It is found in small quantity in argyrodite, a sulphide of silver and germanium, $(3Ag_2S.GeS_2)$, a silver ore from Freiburg, Saxony; euxenite (nisbate and titanate of yttrium, erbium, cerium and uranium) from Sweden (Krüss, *C. C.*, 1888, 75); also contains small amounts of germanium.

3. **Preparation.**—It is formed by reduction of the oxide, GeO_2, with H, C or Mg (Winkler, *B.*, 1891, **24**, 891); also by reduction of the sulphide in H.

4. **Oxides.**—It forms two oxides, GeO and GeO_2. To prepare pure GeO_2, the mineral argyrodite is pulverized and intimately mixed with equal weights of Na_2CO_3 and S and heated to a good full ignition. The mass must be added carefully to prevent foaming. The fused mass is exhausted with H_2O, the germanium going into solution as a thiosalt. With a decided excess of H_2SO_4, the sulphide is completely precipitated. The precipitate is now dissolved in KOH, the sulphides of Ag, Cu and Pb remaining undissolved. By adding to the KOH solution H_2SO_4 not quite to neutralization, the As and Sb sulphides are precipitated on boiling, while the GeS remains in solution with some As_2S_3; H_2S is carefully added to the solution until the As_2S_3 is all precipitated, then the filtrate is made strongly acid with H_2SO_4, and the solution evaporated till SO_3 fumes escape. The mass is dissolved in hot water, and upon cooling GeO_2 crystallizes out (Winkler, *l. c.*).

5. **Solubilities.**—Germanium is insoluble in HCl, soluble in nitrohydrochloric acid as $GeCl_4$, and oxidized with HNO_3 to GeO_2. Hot concentrated H_2SO_4 evolves SO_2 and forms $Ge(SO_4)_2$. Insoluble in KOH solution but dissolves with incandescence in fused KOH. It unites directly with Cl, Br and I (Winkler, *l. c.*). Germanic oxide, GeO_2, is a white powder, very sparingly soluble in water or acids. Fused with fixed alkali hydroxides or carbonates it is converted into compounds soluble in water. $GeCl_4$ is a liquid, boiling at 84°;

it is decomposed by water. If a solution of the oxide in excess of **HCl** be evaporated to dryness the **Ge** is all volatilized. GeS_2 is soluble in 222 parts water, in alkali sulphides and hydroxides; insoluble in **HCl** or H_2SO_4, which precipitate it from its solutions; soluble in nitrohydrochloric acid with separation of sulphur. Nitric oxide changes it to GeO_2 with separation of sulphur.

6. **Reactions.**—Germanium salts give almost no characteristic reactions with the various reagents. H_2S precipitates germanic sulphide, GeS_2, white, from solutions of the salts quite strongly acid. The sulphide is soluble in ammonium sulphide, forming a thio salt, thus placing **Ge** in division A of the second group.

7. **Ignition.**—Heated before the blow-pipe in the reducing flame without an alkaline flux the metal is formed, and at the same time a white coating of the oxide. It forms a colorless bead with borax.

8. **Detection.**—In the mineral, argyrodite, by heating in an atmosphere of H_2S or illuminating gas, an orange-yellow sublimate is obtained, which may be examined under the microscope and in the wet way (Haushofer, *C. C.*, 1888, 867).

9. **Estimation.**—It is converted into the sulphide, GeS_2, and then heated with HNO_3 and weighed as GeO_2.

10. **Oxidation.**—**Zn** in acid solutions of **Ge** salts precipitates the metal as a dark brown slime. If GeS_2 is heated in a current of **H**, **GeS** is at first formed with H_2S, finally **Ge°**.

§112. Tellurium. Te = 127.5. Valence two, four and possibly six.

1. **Properties.**—*Specific gravity*, 6.2445 (Berzelius, *Pogg.*, 1834, **32**, 1 and 577). *Melting point*, 452° (*Cir. B. S.*, **35**, 1915). Te is crystalline, silver white, brittle, stable in the air and in boiling water; heated in the air, it burns with a greenish flame. In its general properties and reactions it stands closely related to **S** and **Se** (2).

2. **Occurrence.**—In few places and in small quantities in Germany, Mexico, Bolivia, United States and Japan. Some of the minerals are: tellurite, (TeO_2); tetradymite ($Bi_2(TeS)_3$); ferrotellurite, ($FeTeO_4$), sylvanite, ($AgAuTe_4$); calaverite, ($AuTe_2$). It also occurs native.

3. **Preparation.**—(*1*) Fusion with alkali carbonate and **C**, which converts it into a telluride, as Na_2Te; then solution in (air free) water, the air being excluded as much as possible, and the filtrate precipitated by passing air through the solution. The **Te** is precipitated as a gray metallic powder, containing what **Se** may have been present. (*2*) Conversion into **TeCl**, by distillation in a current of chlorine, decomposition of the chloride with water to H_2TeO_3 and precipitation of the **Te** with $KHSO_3$. (*3*) From lead chamber scale by digestion with Na_2CO_3 and **KCN**, forming **KCNTe**. The decanted solution is acidified with HNO_3 and the **Te** precipitated with H_2S (Schimose, *C. N.*, 1884, **49**, 157). (*4*) For purification of the commercial **Te**, see Brauner (*M.*, 1889, **10**, 411) and Schimose (*C. N.*, 1884, **49**, 26, and 1885, **51**, 199).

4. **Oxides** and **Hydroxides.**—**TeO** is said to be formed by heating $TeSO_3$ in a vacuum above 180°: $TeSO_3 = TeO + SO_2$ (Divers and Schimose, *C. N.*, 1883, **47**, 221). TeO_2 forms when **Te** is burned in the air, and when $TeCl_4$ is decomposed by boiling water. It is a white crystalline solid, sparingly soluble in H_2O, more soluble in acids from which solutions water causes a white precipitate of TeO_2 or H_2TeO_3. H_2TeO_3 is formed when a HNO_3 solution of **Te** is immediately poured into cold water, warming to 40° changes it to TeO_2. H_2TeO_4 is made by fusing TeO_2 with KNO_3, treating the K_2TeO_4 so obtained with soluble lead or barium salt and decomposing this salt with H_2SO_4 or H_2S, colorless crystals, insoluble in alcohol or ether-alcohol (separation from H_2SO_4). It can be recrystallized from water and upon heating forms TeO_3 (Clarke, *Am. S.*, 1877, **114**, 281; 1878, **116**, 401).

5. **Solubilities.**—**Te** is insoluble in **HCl**; HNO_3 and nitrohydrochloric acids oxidize it to H_2TeO_4; in H_2SO_4 it becomes H_2TeO_3 with evolution of SO_2 (Hilger, *A.*, 1874, **171**, 211); soluble in warm concentrated solution of **KCN**, from which solution **HCl** precipitates all the **Te**. H_2TeO_3 is fairly soluble in water, reddens moist litmus paper and easily decomposes into TeO_2 and H_2O. Acid solu-

tions of TeO_2 are precipitated upon addition of water or upon standing. TeO_2 and H_2TeO_3 form soluble alkali salts with the alkalis from which solutions of the other metallic salts precipitate the respective tellurites. H_2TeO_4 is soluble in water, acids and alkalis; alkali carbonates form acid tellurates, less soluble than the corresponding normal salts. Solutions of the alkali tellurates form insoluble tellurates with soluble salts of the other metals, *e. g.*, $K_2TeO_4 + BaCl_2 = BaTeO_4 + 2KCl$.

6. **Reactions.**—Tellurium is classed with second group metals because of its precipitation from solutions of tellurites and tellurates by H_2S. The precipitate is not a sulphide, but is **Te** mixed with varying proportions of **S**, for CS_2 removes nearly all the sulphur (Becker, *A.*, 1876, **180**, 257). In appearance the precipitate of **Te** with H_2S very much resembles **SnS**, and is very soluble in $(NH_4)_2S$.

At a high temperature **Te** and **H** unite directly, forming H_2Te (Brauner, *M.*, 1889, **10**, 446). H_2Te is best prepared by heating together **Te** and **Fe** or **Zn** and decomposing these tellurides with **HCl** (analogous to the corresponding reactions with sulphur, §**257**, 4). A colorless gas, odor similar to H_2S, burns with a blue flame, fairly soluble in water and is precipitated as **Te°** from its solution by the oxygen of the air. H_2Te precipitates solutions of metallic salts very similarly to H_2S and H_2Se.

7. **Ignition.**—**Te** combines on ignition with most metals to form tellurides. TeO_3 ignited, decomposes into TeO_2 and **O**. All lower **Te** compounds ignited with KNO_3 give K_2TeO_4. All **Te** compounds give on charcoal with the blowpipe a white powder, which colors the reduction flame green and disappears. Heated in an open glass tube, **Te** compounds give a sublimate of TeO_2, which melts upon heating. **Te** compounds fused with **KCN** in a current of hydrogen form potassium tellurocyanate, **KCNTe**; soluble in water but precipitated by a current of air as **Te°** (distinction and separation from **Se**). Heated with Na_2CO_3 on charcoal **Te** compounds give Na_2Te, which blackens silver with formation of Ag_2Te.

8. **Detection.**—By reduction to **Te°** and solution in cold concentrated H_2SO_4 to a purplish-red solution (characteristic). Separated from **Se** by fusion with **KCN** in a current of hydrogen and precipitation from the solution by a current of air.

9. **Estimation.**—The **Te** compound is heated in a current of **Cl**, $TeCl_4$ being sublimed. This is decomposed by water to TeO_2, which is reduced to **Te°** by SO_2 and weighed as such after drying at 100°.

10. **Oxidation.**—Hydrogen at a high temperature reduces **Te** compounds to H_2Te. H_2S reduces **Te** compounds to **Te°** mixed with **S**. Fusion with KNO_3 oxidizes all **Te** compounds to K_2TeO_4. SO_2 reduces **Te** compounds to **Te°**. $SnCl_2$ and **Zn** in acid solutions give with **Te** compounds a black precipitate of **Te°**. **Te** compounds warmed with dextrose in alkaline solution are reduced to **Te°**. Tellurates boiled with **HCl** evolve chlorine and are reduced to H_2TeO_3, which precipitates as TeO_2 on adding water if too much **HCl** be not present (distinction from **Se**).

§113. Selenium. Se = 79.2. Valence two and four, possibly six.

1. **Properties.**—*Specific gravity*, red, cryst., 4.47; gray metallic 4.80; (*J. phys. Chem.* **4**, 491; 1900). *Melting point* 217–220° (*Cir. B. S.*, **35**, 1915). The molten **Se** does not become completely solid until cooled to 50°. Selenium with tellurium is closely related to sulphur, and like sulphur exists in amorphous forms (§**256**, 1). The precipitated **Se** is red. The brown or brown-black powder obtained by quickly cooling from the molten state is insoluble in CS_2. *Boiling point*, 676° to 683° (Carnelley and Williams, *C. N.*, 1879, **39**, 286).

2. **Occurrence.**—In no place abundantly; never native. It is found in combination with minerals in the Hartz Mountains, Sweden, Argentine Republic and Mexico (Billandot, *C. N.*, 1882, **46**, 60). It occurs in very small quantities with some sulphides of **Fe**, **Cu** and **Zn**.

3. **Preparation.**—In the lead chambers of the H_2SO_4 works it is found as a red deposit with some S, As_2O_3, Sb_2O_3, $PbSO_4$, etc. The scale is washed with water and digested with KCN solution at 80° to 100°, until the red color entirely disappears. The filtrate is then treated with HCl, which precipitates the Se. It is further purified by oxidation to SeO_2, sublimed and then reduced with SO_2 (Nilson, *B.*, 1874, **7**, 1719).

4. **Oxides and Hydroxides.**—H_2SeO_3 is prepared by oxidizing Se with HNO_3, or nitrohydrochloric acid. H_2SeO_3 evaporated to dryness gives H_2O and SeO_2, crystalline. SeO_2 is also formed by burning Se in air or oxygen; it has an odor similar to decaying radish. It sublimes at 250°–280° as a yellow vapor, condensing to white needles on cooling. SeO_3 is not known. H_2SeO_4, pure, is a white crystalline mass, melting at 58°. $H_2SeO_4.H_2O$ is crystalline at —38°, and if recrystallized melts at 25°. The selenic acid usually obtained is a thick oily liquid, resembling H_2SO_4 and containing about 95 per cent H_2SeO_4. It is obtained by fusing Se or SeO_2 with KNO_3 and precipitation of the K_2SeO_4 with soluble salts of Ba, Pb, Ca or Cu and decomposing the washed precipitates, suspended in water, with H_2SO_4 or H_2S.

5. **Solubilities.**—Se dissolves in cold concentrated H_2SO_4 to a green colored solution without oxidation (dilution with water precipitates the Se); if the solution be warmed SO_2 is evolved and the green color disappears (dilution with water gives precipitate), the Se being oxidized to SeO_2. HNO_3 and nitrohydrochloric acid oxidize it to SeO_2. Selenous oxide, SeO_2, is soluble in water in all proportions, forming H_2SeO_3. The selenites and selenates of the alkaline earths are insoluble and may be formed by adding a solution of the metal to an alkali selenite or selenate, *e. g.*, $Na_2SeO_3 + BaCl_2 = BaSeO_3 + 2NaCl$. Many of the selenites are soluble in excess of H_2SeO_3. Selenates are less stable than selenites. $BaSeO_4$ is soluble in HCl (distinction and separation from $BaSO_4$) and upon long-continued boiling is reduced to $BaSeO_3$.

6. **Reactions.**—Selenous acid precipitates with H_2S a mixture of Se and S, lemon yellow, bright red upon heating (Divers and Shimose, *C. N.*, 1885, **51**, 199). This mixture is soluble in $(NH_4)_2S$, hence in qualitative analysis Se is classed among the metals of division A, second group, while because of its general properties it belongs with sulphur. When Se and H are heated together they begin to combine directly at 250°, forming H_2Se (Ditte, *C. r.*, 1872, **74**, 980); which in practically all its reactions is similar to H_2S. H_2Se is also formed by treating K_2Se, FeSe, etc., with dilute HCl or H_2SO_4; HNO_3 gives H_2SeO_3 with selenides. H_2Se is a colorless gas, odor similar to H_2S but more penetrating. It is more poisonous than H_2S, burns when ignited, combines slowly but completely with Hg°, evolving hydrogen. 100 cc. of water dissolves 331 cc. of the gas at 13°, the solution reacting acid and depositing red flakes of Se on standing. It precipitates the selenides of the metals having almost the same solubilities as the corresponding sulphides (von Reeb, *J. Pharm.*, 1869, (4), **9**, 173). With soluble sulphites H_2Se gives a precipitate of a mixture of Se and S.

7. **Ignition.**—When Se or compounds of Se are fused with KCN in a current of hydrogen, potassium selenocyanate, KCNSe, is formed. Long boiling with HCl separates the Se, but this does not take place on exposure of the solution to the air (separation from tellurium). Selenium compounds heated on charcoal with Na_2CO_3 are changed to Na_2Se, which yields a black stain with Ag° and H_2Se with dilute acids.

8. **Detection.**—If in solution as selenites it is precipitated with H_2S (soluble in $(NH_4)_2S$); oxidized to SeO_2 and obtained as the white needles by sublimation, and reduced from its solution in water to the red Se° by SO_2. If present as selenides, decomposed by HCl or H_2SO_4, forming H_2Se, which is conducted into water and the Se° precipitated by passing air or oxygen through the solution.

9. **Estimation.**—Oxidized to selenic acid and precipitated as $BaSeO_4$ and weighed as such. If $BaSO_4$ be present the precipitate is reduced in H, and the resulting $BaSeO_3$ separated by solution in HCl. Selenides are heated in a current of chlorine in a hard glass tube, being converted into $SeCl_4$, which vaporizes and is decomposed in water; continued chlorination of the water solution forms H_2SeO_4.

10. **Oxidation.**—Se° is oxidized to SeO_2 by HNO_3, nitrohydrochloric acid,

H_2SO_4 hot concentrated, by heating in air or oxygen, etc. H_2SeO_3 is oxidized to H_2SeO_4 by continued chlorination, and by fusion with KNO_3. H_2SeO_4 is reduced to H_2SeO_3 by boiling with HCl. SO_2 reduces selenous compounds to the red Se°, even in H_2SO_4 solutions (distinction from tellurium) (Keller, *J. Am. Soc.*, 1900, 22, 241). H_2S forms a precipitate of Se mixed with S. $SnCl_2$ precipitates Se° from HCl or H_2SO_4 solutions of selenous compounds.

The Iron and Zinc Groups (Third and Fourth Groups).

§114. The Metals of the Earths and the more Electro-Positive of the Heavy Metals.

Aluminum	Al	27.1	Neodymium	Nd	144.3
Chromium	Cr	52.0	Praseodymium	Pr	140.9
Iron	Fe	55.84	Samarium	Sa	150.4
Cobalt	Co	58.97	Scandium	Sc	44.1
Nickel	Ni	58.68	Tantalum	Ta	181.5
Manganese	Mn	54.93	Terbium	Tb	159.2
Zinc	Zn	65.37	Thallium	Tl	204.00
Cerium	Ce	140.25	Thorium	Th	232.4
Columbium	Cb	93.5	Titanium	Ti	48.10
Erbium	E	167.7	Uranium	U	238.2
Gallium	Ga	69.9	Vanadium	V	51.0
Glucinum	Gl	9.1	Ytterbium	Yb	173.5
Indium	In	114.8	Yttrium	Y	188.7
Lanthanum	La	139.0	Zirconium	Zr	90.6

§115. The metals above named gradually oxidize at their surfaces in the air, and their oxides are not decomposed by heat alone. Zinc, iron, cobalt, nickel, and, with more difficulty, manganese, chromium, and most of the other metals of the groups, are reduced from their oxides by ignition at white heat with charcoal. They are all reduced from oxides by the alkali metals. Iron is gradually changed from ferrous to ferric combinations by contact with the air. Chromium and manganese are oxidized from bases to acid radicals by ignition with an active supply of oxygen in presence of alkalis; these acid radicals acting as strong oxidizing agents (§8, §9).

§116. The *oxides* and *hydroxides* of these metals are **insoluble** in water and they are precipitated from all their salts by **alkalis.** In the case of *zinc*, the precipitate redissolves in all the alkalis; the *aluminum* hydroxide redissolves in the fixed alkalis, but very slightly in ammonium hydroxide; the precipitate of *chromium* redissolves in cold solution of fixed alkalis, precipitating again on dilution and boiling; the hydroxides of *cobalt* and *nickel* dissolve in ammonium hydroxide. The oxide of chromium after ignition is insoluble in acids; the oxides of aluminum and iron are soluble with difficulty.

The presence of tartaric acid, citric acid, sugar, and some other **organic substances,** *prevents the precipitation of bases of these groups by alkalis.*

§117. **Ammonium salts**, as NH_4Cl, dissolve moderate quantities of the hydroxides of manganese, zinc, cobalt, nickel, and ferrous hydroxide; but, so far from dissolving the hydroxide of aluminum, they lessen its slight solubility in ammonium hydroxide.

§118. It thus appears that **ammonium hydroxide**, with **ammonium chloride**, the latter necessary on account of magnesium (§189, 6*a*), manganese (§134, 6*a*), and aluminum, will fully precipitate only **aluminum, chromium,** and **iron** of the important metals above named. These metals therefore constitute the THIRD GROUP (§127), and the reagent of this group is AMMONIUM HYDROXIDE in the presence of AMMONIUM CHLORIDE. Since **aluminum, chromium,** and **iron** are precipitated by ammonium hydroxide in the presence of ammonium chloride (**Fe**″ by its previous oxidation with HNO_3 is present as **Fe**‴) constituting the THIRD GROUP; the remaining of the most important metals—**cobalt, nickel, manganese,** and **zinc**—constitute the FOURTH GROUP (§137). They are precipitated by the group reagent, AMMONIUM SULPHIDE or HYDROSULPHURIC ACID in an AMMONIACAL SOLUTION. Some chemists do not make this classification of these metals, but precipitate them all as one group with **ammonium sulphide** (§144), from neutral or ammoniacal solutions. The sulphides of **Fe**, **Co**, **Ni**, **Mn**, and **Zn** are not formed in presence of dilute acids, which acids keep them in solution during the second group precipitation; but are insoluble in water, which enables them to be precipitated by alkali sulphides, and separated from the fifth and sixth groups. The other two metals, **Al** and **Cr**, do not form sulphides, in the wet way, but are precipitated as hydroxides by the alkali sulphides.

§119. **Hydrosulphuric acid** scarcely precipitates the metals of these groups, unless it be from some of their acetates (§135, 6*c*), owing to the solubility of the sulphides in the acids, which would be set free in their formation. Thus, this change cannot occur—$FeCl_2 + H_2S = FeS + 2HCl$—because the two products would decompose each other. Hydrogen sulphide does not precipitate the metals of these groups in acid solution unless the acid is very weak (acetic acid §135, 6*c*). The hydrogen ions of strong acids, which are largely dissociated, reduce the concentration of the sulphur ion of the hydrogen sulphide below the point where it can precipitate the sulphides of these metals. For the same reason these sulphides are dissolved by strong acids and the reaction $FeCl_2 + H_2S \rightleftarrows FeS + 2HCl$ cannot proceed from right to left.

As acetic acid and other weak acids are only slightly dissociated, the concentration of the hydrogen ion is very much less and the decrease in the concentration of the sulphur ion of the hydrogen sulphide is slight. The soluble sulphides are dissociated to a much greater extent giving a con-

centration of the sulphur ion sufficient to precipitate the sulphides of these metals. (See **45**.) Therefore when it is desired to precipitate the metals as **sulphides**, neutralized **hydrosulphuric acid**—an *alkali sulphide*—is used in *neutral* or *alkaline* solution; or, what is equivalent, **hydrosulphuric acid gas** is passed into the *strongly ammoniacal solution*.

§120. As most of the *normal chemically* salts of heavy metals are hydrolyzed, in water, giving free acids, so that their solutions have an acid reaction to test-paper, we can only assure ourselves of the requisite neutrality by adding sufficient ammonium hydroxide, which itself precipitates the larger number of the bases, as we have just seen (§**116**). But the resulting precipitate of hydroxide, as $Fe(OH)_2$, is immediately changed to sulphide, **FeS**, by subsequent addition of ammonium sulphide; as the student may observe, by the change in the color of the precipitate.

Ferric and manganic salts are **reduced** to ferrous and manganous salts, by hydrosulphuric acid, in solution, with a *precipitation of sulphur*, and the corresponding reaction occurs with chromates.

§121. Soluble **carbonates** precipitate all the metals of these groups, in accordance with the general statement for bases not alkali (§**205**, 6*a*). With aluminum and chromium, the precipitates dissolve sparingly in excess of potassium or sodium carbonate; with **Co**, **Ni** and **Zn**, the precipitate dissolves in excess of $(NH_4)_2CO_3$. In the case of ferrous and manganous salts, the precipitates are normal carbonates; with zinc, cobalt, and nickel salts, they are basic carbonates; while with ferric, aluminum, and chromium salts, the precipitates are hydroxides. Barium carbonate precipitates **Al**, Cr''' and Fe''', which, in the cold and from salts not sulphates, is a separation from the fourth group metals.

§122. Soluble **phosphates** precipitate these as they do other non-alkali bases. The acid solutions of phosphates of the metals of the third and fourth groups are precipitated by neutralization. Phosphates of **Co**, **Ni**, and **Zn** are redissolved by excess of NH_4OH, and those of **Al**, **Cr**, and **Zn** by excess of the fixed alkalis. The recently precipitated phosphates of all the metals of these groups which form sulphides, are transformed to sulphides by ammonium sulphide, due to the fact that the sulphide is less soluble than the phosphate: $FeHPO_4 + (NH_4)_2S = FeS + (NH_4)_2HPO_4$. Hence, the only phosphates which may occur in a sulphide precipitate are those of **Al**, **Cr**, **Ba**, **Sr**, **Ca**, and **Mg**.

§123. The metals of the third and fourth groups are not easily reduced from their compounds to the metallic state by **ignition** before the blow-pipe, even *on charcoal*, except zinc, which then vaporizes. Three of them, however—iron, cobalt, and nickel—are reducible to magnetic oxides. The larger number of them give characteristic colors to **beads** of borax and of microcosmic salt, fused on a loop of platinum wire before the blow-pipe.

None of them color the flame or give spectra, unless vaporized by a higher temperature than that of a Bunsen burner (spark spectra).

The Iron Group (Third Group).

Aluminum, Chromium, Iron.

§124, Aluminum. Al = 27.1. Valence three.

1. **Properties.**—*Specific gravity*, 2.708 (*C. N.*, 105, 1912). The cast metal has specific gravity of 2.56. *Melting point*, 658.7° (*Cir. B. S.*, **35**, 1915). It is a tin-white metal (the powder is gray), odorless and tasteless, very ductile and malleable, about as hard as silver. Its boiling point is above 2200°. Impurities increase the melting point. When molten it possesses great fluidity. As a conductor of heat it is about twice as good as tin and about one-third as good as silver. It conducts electricity about one-half as well as copper and silver (Dewar and Fleming, *Phil. Mag.*, (5) **36**, 271, 1893. Roy, *Inst. Gt. Brit.*, June 5, 1896), and about three times better than iron. Commercial aluminum is never pure, containing small amounts of silicon and iron, and sometimes **Cu** and **Pb**, with 96 to 99.75 per cent aluminum. It is used for cooking utensils, canteens and other military equipments, boats, small weights, measures, articles of ornament and scientific instruments; as an alloy with copper (aluminum bronze) it finds extensive application.

2. **Occurrence.**—Not found free in nature. Is found in corundum, ruby and sapphire, as nearly pure Al_2O_3; in diaspore ($Al(OH)_3.Al_2O_3$); in bauxite ($Al_2O_3.xH_2O$); in orthoclase ($KAlSi_3O_8$), and other feldspars; in cryolite (Na_3AlF_6). As a silicate in all clays and in very many minerals. It is widely distributed, constituting about one-twelfth of the earth's crust.

3 **Preparation.**—(*1*) By electrolysis of the fused $NaAlCl_4$. (*2*) By fusion of cryolite or the chloride with **Na** or **K**. (*3*) By heating $NaAlCl_4$ with zinc, with which it forms an alloy from which the zinc is driven off by a white heat. (*4*) By fusion of the chloride with potassium cyanide. (*5*) By fusing Al_2S_3 with iron. A great many new methods have been patented. (*6*) Aluminum is prepared commercially, by electrolysis of aluminum oxide dissolved in a bath of cryolite (Na_3AlF_6). The metal is deposited around the cathode, oxygen being evolved at the anode. See Dammer, **3**, 79.

4. **Oxide** and **Hydroxides.**—Al_2O_3 is formed by heating the hydroxide, nitrate, acetate or other organic salt, difficultly soluble in acids after ignition, but may be dissolved after fusion with $KHSO_4$ or Na_2CO_3. $Al(OH)_3$ is formed when aluminum salts are precipitated with cold ammonium hydroxide. $Al_2O(OH)_4$ is formed if the precipitation is made at 100°.

5. **Solubilities.**—*a.—Metal.*—Pure aluminum scarcely oxidizes at all in dry or moist air; the electrolytically deposited powder oxidizes gradually in the air. Powdered or leaf aluminum when boiled with water evolves hydrogen, forming the hydroxide. It is attacked by the halogens forming the corresponding halides (Gustavson, *Bl.*, 1881, (2), **36**, 556). Dilute sulphuric acid attacks it slowly, evolving hydrogen (Ditte, *C. r.*, 1890, **110**, 573); the hot concentrated acid dissolves it readily with evolution of SO_2. Nitric acid, dilute or concentrated, attacks it very slowly (Deville, *A. Ch.*, 1855, (3), **43**, 14; Montemartini, *Gazzetta*, 1892, **22**, 397; Ditte, *l. c.*, 782). Hydrochloric acid, dilute or concentrated, dissolves it readily with evolution of hydrogen; also attacked readily by fixed alkalis, sparingly by NH_4OH (Göttig, *B.*, 1896, **29**, 1671), evolving hydrogen with formation of an aluminate: $2Al + 2KOH + 2H_2O = 2KAlO_2 + 3H_2$. It is attacked by fixed alkali carbonates (*D.*, **3**, 87). When ignited with sodium carbonate, aluminum oxide is formed, sodium is vaporized and a small amount of aluminum nitride produced (Mallet, *J. C.*, 1876, **30**, 349). Fused **KOH** is decomposed by aluminum at very high temperature, the potassium being vaporized (Deville, *J.*, 1857, 152). It is not at all attacked by cold four per cent acetic acid (vinegar) even in presence of **NaCl**, and when boiled for

14 hours with the above mixture a square meter of surface (weighing 24.7426 grams) lost but 0.047 gram (one part in 526).

b.—**Oxide** and **hydroxide.**—The oxide is insoluble in water, and when not too strongly ignited dissolves readily in dilute acids and in fixed alkalis. Corundum, crystallized Al_2O_3, is insoluble in acids, but is rendered soluble by fusion in fixed alkali carbonates or sulphates. The hydroxide $Al(OH)_3$ is insoluble in water, readily soluble in acids and in fixed alkalis, sparingly soluble in ammonium hydroxide, the solubility, however, being much decreased by the presence of ammonium salts. *c.*—*Salts.*—Aluminum phosphate is insoluble in water. The normal acetate is soluble, the basic acetate insoluble in water (separation from **Cr** and the fourth group). The chloride is *deliquescent*. The double sulphates of aluminum and the alkali metals (alums) are soluble and readily melt in their water of crystallization, becoming anhydrous. Solutions of normal salts of aluminum have an acid reaction.

6. **Reactions.** *a.*—The **alkali hydroxides** and **carbonates** * precipitate aluminum hydroxide (*1*), $Al(OH)_3$ (4), grayish-white, gelatinous insoluble in water, soluble in excess of the fixed alkali hydroxides † (*2*) (Prescott, *J. Am. Soc.*, 1880, **2**, 27; Ditte, *A. Ch.*, 1897 (6), **30**, 266), sparingly soluble in the fixed alkali carbonates and in ammonium hydroxide but *much* less so if ammonium salts be present. The solution of fixed alkali aluminate is precipitated as aluminum hydroxide by careful neutralization of the alkali with acids including hydrosulphuric (*3*), and carbonic, as basic hydroxide, by adding excess of ammonium chloride (*4*) (distinction from zinc which is precipitated by a small amount of NH_4Cl, but redissolves on adding an excess) (Löwe, *Z.*, 1865, **4**, 350). The excess of potassium hydroxide liberates ammonia forming potassium chloride, thus reducing the amount of fixed alkali present. The precipitate is more compact and washes more readily than the gelatinous normal hydroxide. **Barium carbonate**, on digestion in the cold for some time completely precipitates aluminum salts as the hydroxide (*5*) mixed with a little basic salt. (See §126, 6*a*.) The presence of citric, oxalic, or tartaric acid greatly hinders the precipitation of aluminum hydroxide, and an excess may entirely prevent its precipitation by the formation of a soluble double salt, *e. g.*, $KAl(C_4H_4O_6)_2$. Other organic substances, as sugar, pieces of filter paper, etc., hinder the precipitation. To obtain complete precipitation all organic substances should be decomposed.

(*1*) $AlCl_3 + 3KOH = Al(OH)_3 + 3KCl$

$2AlCl_3 + 3K_2CO_3 + 3H_2O = 2Al(OH)_3 + 6KCl + 3CO_2$

(*2*) $Al(OH)_3 + KOH = KAlO_2 + 2H_2O$

or $AlCl_3 + 4KOH = KAlO_2 + 3KCl + 2H_2O$

(*3*) $2KAlO_2 + H_2S + 2H_2O = 2Al(OH)_3 + K_2S$

(*4*) $2KAlO_2 + 2NH_4Cl + H_2O = Al_2O(OH)_4 + 2KCl + 2NH_3$

(*5*) $2AlCl_3 + 3BaCO_3 + 3H_2O = 2Al(OH)_3 + 3BaCl_2 + 3CO_2$

* According to Langlois (*A. Ch.*, 1856, (3), 48, 502) the precipitate with alkali carbonates always contains CO_2. He assigns the formula $3(Al_2O_3CO_2) + 5(Al_2O_3.8H_2O)$.

† A solution of barium hydroxide may be used to dissolve the $Al(OH)_3$ in separating from $Fe(OH)_3$ and $Cr(OH)_3$; especially valuable in detecting the presence of small amounts of aluminum when the reagents **NaOH** and **KOH** contain aluminum (Neumann, *M.*, 1894, **15**, 53).

b.—**Oxalates** do not precipitate aluminum salts. The *acetate* of *aluminum* is decomposed upon boiling, forming the insoluble basic acetate (separation of iron and aluminum from the fourth group): $Al(C_2H_3O_2)_3 + H_2O = Al(C_2H_3O_2)_2OH + HC_2H_3O_2$. The basic acetate is best formed as follows: To the solution of aluminum salt add a little sodium or ammonium **carbonate**, as much as can be added without leaving a precipitate on stirring, then add excess of **sodium or ammonium acetate**, and boil for some time, when the precipitation at length becomes very nearly complete.

Phenyl hydrazine, $C_6H_5NHNH_2$, completely precipitates aluminum as the hydroxide from the neutral solution of its salts (complete separation of aluminum and chromium from iron which should be in the ferrous condition) (Hess and Campbell, *J. Am. Soc.*, 1899, **21**, 776).

c.—**Nitric acid** is a very poor solvent for metallic aluminum, but a good solvent for the oxide and hydroxide. The metal dissolves in a solution of the normal aluminum nitrate, evolving hydrogen and forming the basic nitrate $Al_4O_5(NO_3)_2$ (Ditte, *C. r.*, 1890, **110**, 782).

d.—**Alkali phosphates** precipitate aluminum phosphate, $AlPO_4$, white, insoluble in water and acetic acid, soluble in mineral acids, and in the fixed alkalis (separation from $FePO_4$) (Grueber, *Z. angew.*, 1896, 741). A separation of **Al** and PO_4 may be effected by dissolving in hydrochloric acid adding tartaric acid and then ammonium hydroxide, and digesting some time with magnesia mixture (magnesium sulphate to which sufficient ammonium chloride has been added so that no precipitate is obtained when rendered strongly alkaline with ammonium hydroxide). The filtrate contains nearly all of the aluminum. The same method may be employed with Fe''' and PO_4. See also 7.

e.—The **sulphide** of aluminum cannot be prepared in the wet way, that prepared in the dry way being decomposed by water (Curie, *C. N.*, 1873, **28**, 307). **Hydrosulphuric acid** does not precipitate aluminum from acid or neutral solutions; from its solutions in the fixed alkalis it is precipitated as the hydroxide on addition of sufficient hydrosulphuric acid to neutralize the fixed alkali (distinction from zinc which is rapidly precipitated from its alkaline solutions, as the sulphide). The alkali sulphides precipitate aluminum from its solutions, as the hydroxide; from acid or neutral solution H_2S is evolved: $2AlCl_3 + 3(NH_4)_2S + 6H_2O = 2Al(OH)_3 + 6NH_4Cl + 3H_2S$, from solutions in the fixed alkalis ammonia is evolved, fixed alkali sulphide being formed: $2KAlO_2 + (NH_4)_2S + 2H_2O = 2Al(OH)_3 + K_2S + 2NH_3$.

Sodium thiosulphate precipitates, from aluminum salts, in neutral solutions, aluminum hydroxide with free sulphur and liberation of sulphurous anhydride: $2Al_2(SO_4)_3 + 6Na_2S_2O_3 + 6H_2O = 4Al(OH)_3 + 3S_2 + 6Na_2SO_4 + 6SO_2$. A small amount of sodium tetrathionate is formed and also some hydrosulphuric acid (Vortmann, *B.*, 1889, **22**, 2307). **Sodium sulphite** also precipitates alu-

minum hydroxide, with liberation of sulphur dioxide: $2AlCl_3 + 3Na_2SO_3 + 3H_2O = 2Al(OH)_3 + 6NaCl + 3SO_2$. Neither of the above reagents precipitate iron salts, thus effecting a separation of aluminum (and chromium) from iron.

Aluminum, chromium and ferric sulphates crystallize with the sulphates of the alkali metals, forming a class of compounds, ALUMS, of which the potassium aluminum compound is perhaps best known, $KAl(SO_4)_2.12H_2O$, *common alum*. These compounds melt in their water of crystallization, becoming anhydrous upon further heating. The freshly ignited alum is only sparingly soluble in cold water, but upon standing becomes readily soluble, dissolving in less than one part of hot water. The alums are usually less soluble than their constituent sulphates and may be precipitated by adding a saturated solution of alkali sulphate to a very concentrated solution of Al, Cr''', or Fe''' sulphate.

f.—Aluminum **chloride** is a very powerful dehydrating agent and is much used in organic chemistry as a halogen carrier. An impure aluminum chlorate, mixture of $KClO_3$ and $Al_2(SO_4)_3$, is much used in calico printing (Schlumberger, *Dingl.*, 1873, **207**, 63). *g*.—Aluminum salts are precipitated by solutions of alkali arsenites and arsenates, but not by arsenous or arsenic acids. *h*.—Potassium chromate forms a yellow gelatinous precipitate, potassium bichromate gives no precipitate with aluminum salts. *i*.—Solution of borax precipitates an acid aluminum borate, quickly changed to aluminum hydroxide.

7. **Ignition.**—Compounds of aluminum are not reduced to the metal, but most of them are changed to the oxide, by **ignition** on charcoal. If now this residue is moistened with solution of **cobaltous nitrate**, and again strongly ignited, it assumes a *blue* color. This test is conclusive only with infusible compounds, and applies only in absence of colored oxides. Aluminum compounds ignited on charcoal in presence of sulphur are changed to Al_2S_3 (Buchererer, *Z. angew.*, 1892, 483).

To separate Al *from* PO_4, fuse the precipitate or powdered substance with 1½ parts finely divided **silica** and 6 parts dried **sodium carbonate** in a platinum crucible, for half an hour. Digest the mass for some time in water; add **ammonium carbonate** in excess, filter and wash. The residue consists of aluminum sodium silicate; the solution contains the PO_4, as sodium phosphate. The Al can be obtained from the residue by dissolving it in **hydrochloric acid**, evaporating to dryness to render the silica insoluble. Treat with hydrochloric acid and filter; the filtrate containing aluminum chloride.

8. **Detection.**—After the removal of the first two groups it is precipitated with Cr and Fe''' as the hydroxide, $Al(OH)_3$, by NH_4OH in the presence of NH_4Cl. It is separated from $Fe(OH)_3$ and $Cr(OH)_3$ by boiling with KOH or NaOH or by fusion with an alkaline oxidizing agent such as NaClO or Na_2O_2. From the filtrate acidulated with HCl it is precipitated as hydroxide with $(NH_4)_2CO_3$; or it is precipitated from the alkaline solution by an excess of NH_4Cl (*6a*).

9. **Estimation.**—Aluminum is usually weighed as the oxide, after ignition It is separated from zinc as a basic acetate; from chromium by oxidizing the latter to chromic acid, by boiling with potassium chlorate and nitric acid, or by fusing with KNO_3 and Na_2CO_3, or by action of Cl or Br in presence of KOH, or by Na_2O_2 fused or in solution, and after acidulating with HCl precipi-

tating the aluminum with ammonium hydroxide. It may be separated from iron by boiling with **KOH** (6a), by $Na_2S_2O_4$ (6e), or by phenylhydrazine (6b). It is separated from iron by conversion into the oleate and dissolving the oleate of iron (**Fe‴** or **Fe″**) in petroleum (Borntraeger, Z., 1893, **32**, 187). It is sometimes precipitated and weighed as the phosphate.

10. **Oxidation.**—Aluminum reduces solutions of **Pb**, **Ag**, **Hg** *, **Sn**, **Bi** (incompletely), **Cu** †, **Cd**, **Co**, **Ni**, **Zn** ‡ and **Gl** (in alkaline mixture only), **Te**, **Se**, **Au**, and **Pt**, to the metallic state; ferric salts to ferrous salts; **As** and **Sb** with **HCl** become respectively AsH_3 and SbH_3, with alkalis **As‴** is reduced to AsH_3. As^V is unchanged (§**69**, 6*b* and 10), and **Sb‴** and Sb^V become **Sb°**. Aluminum salts are not reduced to the metallic state by any other compounds at ordinary temperature; by fusion with **K** or **Na** metallic aluminum is obtained, much better, however, by the aid of the electric current.

§125. Chromium. Cr = 52.0. Valence two, three and six.

1. **Properties.**—*Specific gravity*, 6.92 (Moissan, *C. r.*, 116). Melting point 1520° (*Cir. B. S.*, **35**, 1915). A grayish-white crystalline metal. The hardness of steel is greatly increased by the presence of less than one per cent of chromium. It is non-magnetic (Woehler, *A.*, 1859, **111**, 231). It burns to the oxide Cr_2O_3 when heated to 200° to 300° in the air (Moissan, *C. r.*, 1879, **88**, 180).

2. **Occurrence.**—Not found native. Chrome-ironstone or chromite ($FeOCr_2O_3$) is the chief ore of chromium, and is usually employed in the manufacture of chromium compounds. Chromite and also Daubréelite ($FeCr_2S_4$), are frequently found in meteorites; it also occurs in crocoite ($PbCrO_4$), and other rare chromates and sulphates.

3. **Preparation.**—(*1*) By electrolysis of the chloride. (*2*) By fusing the chloride with potassium or sodium. (*3*) By ignition of the oxide with carbon. (*4*) By fusing $CrCl_3$ with **Zn**, **Cd** or **Mg**, using **KCl** and **NaCl** as a flux, and removing the excess of the **Zn**, **Cd** or **Mg** by dissolving in nitric acid, which does not dissolve metallic chromium. (*5*) By ignition of the oxide with aluminum (Goldschmidt, *A.*, 1898, **301**, 19).

4. **Oxides** and **Hydroxides.**—*Chromous oxide*, **CrO**, has not been isolated. The corresponding *hydroxide*, $Cr(OH)_2$, is made by treating $CrCl_2$ with **KOH**. *Chromic oxide*, Cr_2O_3, is made by a great variety of methods, among which are fusing the nitrate, or higher or lower oxides and hydroxides in the air; heating mercurous chromate, or the dichromates of the alkalis:

$$4Hg_2CrO_4 = 2Cr_2O_3 + 8Hg + 5O_2$$
$$(NH_4)_2Cr_2O_7 = Cr_2O_3 + N_2 + 4H_2O$$
$$4K_2Cr_2O_7 = 2Cr_2O_3 + 4K_2CrO_4 + 3O_2$$

In the last the K_2CrO_4 may be separated by water. After heating to redness, Cr_2O_3 is insoluble in acids. *Chromic hydroxide*, $Cr(OH)_3$, is precipitated by adding NH_4OH to chromic solutions. That formed by precipitating with **KOH** or **NaOH** retains traces of the alkali, not easily removed by washing.

Chromium trioxide or chromic anhydride, CrO_3, is formed as brown-red needles upon addition of concentrated sulphuric acid to a concentrated solution of $K_2Cr_2O_7$; to be freed from sulphuric acid it must be recrystallized from water, in which it is readily soluble, or treated with the necessary amount of

* Klandy, *C. C.*, 1893, 201; Wislicenus, *B.* 1895, **28**, 1323.
† Tommasi, *Bl.*, 1882, (2), **37**, 443.
‡ Flavitsky, *B.*, 1873, **6**, 195; Zimmerman, *Z.*, 1888, **27**, 61.

$BaCrO_4$ (Moissan, *A. Ch.*, 1885, (6), **5**, 568). It is also prepared by transposition of $BaCrO_4$ with HNO_3 or H_2SO_4; $PbCrO_4$ with H_2SO_4; and Ag_2CrO_4 with **HCl**; etc. It melts at 196°, decomposing at higher temperature into Cr_2O_3 and **O**. It is used in dyeing silk and wool, but not cotton fabrics. It is a powerful oxidizing agent, being reduced to chromic oxide. The existence of chromic acid, H_2CrO_4, is disputed (Moissan, *l. c.*; Field, *C. N.*, 1892, **65**, 153; and Ostwald, *Zeit. phys. Ch.*, 1888, **2**, 78). Two series of salts are formed as if derived from chromic acid, H_2CrO_4, and dichromic acid, $H_2Cr_2O_7$. The salts are quite stable and find an extended application in analytical chemistry (6*h*, §57, §59, §186, etc.).

5. **Solubilities.**—*a.*—*Metal.*—Chromium is not at all oxidized by water or moist air at 100°. Heated above 200° it is oxidized to Cr_2O_3, rapidly in presence of **KOH**. It is soluble in **HCl** or dilute H_2SO_4; insoluble in concentrated H_2SO_4 or in HNO_3, dilute or concentrated. Chlorine or bromine attack it with formation of the corresponding halides (Woehler, *l. c.*; Ufer, *A.*, 1859, **112**, 302). *b.*—**Oxides** and **Hydroxides.**—*Chromic oxide*, Cr_2O_3, is insoluble in water, slowly soluble in acids, but not at all if previously ignited (Traube, *A.*, 1848, **66**, 88); the *hydroxide* is insoluble in water, soluble in acids, sparingly soluble in ammonium hydroxide, soluble in fixed alkalis to chromites, reprecipitated again upon boiling. The presence of other metallic hydroxides, as iron, etc., hinders the solution in fixed alkalis. Chromic anhydride, CrO_3, is very soluble in water, soluble in reducing acids to chromic salts.

c.—*Salts.*—Chromic sulphide is not formed in the wet way, being decomposed by water; the phosphate is insoluble in water. The chloride exists in two modifications; a *deliquescent* soluble chloride, which also forms a soluble basic chloride (Ordway, *Am. S.*, 1858 (2), **26**, 202); and a violet sublimed chromic chloride absolutely insoluble in water, hot or cold, or in dilute or concentrated acids, the presence of a very small amount of chromous or stannous chloride at once renders this modification soluble in water (Peligot, *A. Ch.*, 1846 (3), **16**, 298); the bromide and sulphate also exist in soluble and insoluble modifications; the nitrate and also the basic nitrates are readily soluble in water (Ordway, l. c.). There are many double salts, the sulphates of chromium and the alkali metals, chrome alum, forming salts similar to the corresponding aluminum compounds. There are two modifications of solutions of chromium salts, one having a green color and the other violet to red, the tints being modified somewhat by the degree of the concentration. All normal chromic salts in solution have an acid reaction, being partially hydrolized.

6. **Reactions.*** *a.*—**Alkali hydroxides** and **carbonates** precipitate solutions of chromic salts, as *chromium hydroxide,* gelatinous, gray-green or gray-blue according to the variety of solution from which it is obtained (5*c*), insoluble in water, soluble in acids; soluble in excess of the fixed alkalis to chromites: $Cr(OH)_3 + KOH \rightleftarrows KCrO_2 + 2H_2O$. This reaction

*Chromous salts are very unstable, they are great reducing agents, oxidizing rapidly when exposed to the air. They are almost never met with in analysis. Chromous chloride, $CrCl_2$, is formed when the metal is heated in contact with hydrochloric acid gas (Ufer, *l. c.*); also by reduction of $CrCl_3$ with hydrogen in a heated tube (Moberg, *J. pr.*, 1848, **44**, 322). Precipitates are formed in its solutions by the alkali hydroxides, carbonates, sulphides, etc. (Moissan, *Bl.*, 1882 (2), **37**, 296).

is reversible. The **KOH** tends to form, while the water, especially when hot, tends to decompose the chromite. The chromium may therefore be reprecipitated from this solution if the excess of **KOH** is small and the solution is diluted and boiled. (Distinction from aluminum.) As ammonium chloride reacts with the caustic potash forming potassium chloride and the weak alkali, ammonium hydroxide, the chromium may also be precipitated by the addition of ammonium chloride and heating. The presence of ferric hydroxide and some other compounds greatly hinders the solution in fixed alkalis, hence chromium cannot be separated from iron by excess of fixed alkali. Chromium hydroxide is slightly soluble in excess of cold ammonium hydroxide to a violet solution, completely reprecipitated on boiling. The precipitate formed with the alkali carbonates is almost entirely free from carbonate: $2CrCl_3 + 3Na_2CO_3 + 3H_2O = 2Cr(OH)_3 + 6NaCl + 3CO_2$. Barium carbonate precipitates chromium from its solutions (better from the chloride) as a hydroxide with some basic salt, the precipitation being complete after long digestion in the cold (separation from the fourth group). For removal of excess of reagent, add H_2SO_4 and the filtrate will contain the chromium as a sulphate.

Alkali dichromates are changed to normal chromates by alkali hydroxides or carbonates.

b.—Chromium forms no **basic acetate** and remains in solution when the basic acetates of aluminum and ferric iron are formed (*6b*, §124 and §126). **Potassium cyanide** precipitates chromium hydroxide. **Oxalates** and **ferrocyanides** cause no precipitate. H_2CrO_4 is reduced to chromic compounds by $K_3Fe(CN)_6$ and **KCNS**. *c*.—Nitrites or **nitrates** are without action upon chromium salts in the wet way, but upon fusion in presence of nitrites or nitrates and alkali carbonate a chromate is formed (separation from **Fe** and **Al**). *d*.—**Hypophosphorous acid** reduces chromates to chromic salts. Soluble **phosphates**, as Na_2HPO_4, precipitate chromic phosphate, $CrPO_4$, insoluble in acetic acid, decomposed by boiling with **KOH**, leaving the phosphate in solution (Kammerer, *J. C.*, 1874, **27**, 1005).

e.—**Hydrosulphuric acid** is without action upon neutral or acid solutions of chromic salts, chromites as $KCrO_2$ are precipitated as chromium hydroxide; $2KCrO_2 + H_2S + 2H_2O = 2Cr(OH)_3 + K_2S$. The hexad chromium of chromates is reduced to the triad condition with liberation of sulphur, in neutral or alkaline solutions, chromium hydroxide being formed: $2K_2Cr_2O_7 + 8H_2S = 4Cr(OH)_3 + 2K_2S + 3S_2 + 2H_2O$; in acid solutions a chromic salt is formed (10). Alkali **sulphides** precipitate chromic salts as the hydroxide liberating H_2S:

$$2CrCl_3 + 3(NH_4)_2S + 6H_2O = 2Cr(OH)_3 + 6NH_4Cl + 3H_2S$$

Chromates are reduced and precipitated as chromium hydroxide with separation of sulphur: $4K_2CrO_4 + 6(NH_4)_2S + 4H_2O = 4Cr(OH)_3 + 8KOH$

$+ 3S_2 + 12NH_3$. Soluble **sulphites** and **thiosulphates** reduce chromates in acid solution (Donath, *J. C.*, 1879, **36**, 401; Longi, *Gazzetta*, 1896, **26**, ii, 119).

f.—**Hydrochloric acid** reduces chromates to chromic chloride on boiling, with evolution of chlorine: $2K_2CrO_4 + 16HCl = 2CrCl_3 + 4KCl + 3Cl_2 + 8H_2O$; more readily without evolution of chlorine in presence of other easily oxidized agents, as alcohol, oxalic acid, etc.: $K_2Cr_2O_7 + 8HCl + 3C_2H_5OH = 2KCl + 2CrCl_3 + 3C_2H_4O$ (acetaldehyde) $+ 7H_2O$. If the dry chromate be heated with sulphuric acid and a chloride (transposable by sulphuric acid) (§**269**, 5), brown fumes of chromium dioxydichloride are evolved: $K_2Cr_2O_7 + 4NaCl + 3H_2SO_4 = 2CrO_2Cl_2 + K_2SO_4 + 2Na_2SO_4 + 3H_2O$ (§**269**, 8*d*) (Moissan, *Bl.*, 1885 (2), **43**, 6). To obtain a quantity of CrO_2Cl_2, Thorpe (*J. C.*, 1868, **21**, 514) recommends 10 parts of **NaCl** and 12 parts $K_2Cr_2O_7$ fused together and distilled with 30 parts of H_2SO_4. **Hydrobromic acid** reduces chromates to chromic bromide with evolution of bromine; **hydriodic acid** to chromic iodide with evolution of iodine. In the presence of hydrochloric or sulphuric acids all the bromine or iodine is set free. $K_2Cr_2O_7 + 6HI + 4H_2SO_4 = K_2SO_4 + Cr_2(SO_4)_3 + 3I_2 + 7H_2O$. Hydriodic acid acts most readily upon chromates, the hydrochloric least readily. Chromic hydroxide and chromic salts, when boiled with chloric or bromic acids, or potassium chlorate or bromate and nitric, sulphuric or phosphoric acids, become chromic acid.

g.—Soluble **arsenites** and **arsenates** form corresponding salts with chromic salts. Chromates in acid solution are instantly reduced to chromic salts by arsenites or arsenous acid. Chromic acid boiled with arsenous acid in excess gives $CrAsO_4$ (Neville, *J. C.*, 1877, **31**, 283).

h.—Potassium chromate colors an acid solution of chromic salt brown-yellow; on addition of ammonium hydroxide, a precipitate of the same color is obtained, chromic chromate (Maus, *Pogg.*, 1827, **9**, 127). The alkali metals form two classes of chromates: yellow normal chromates and reddish dichromates (Schulernd, *J. C.*, 1879, **36**, 298). The chromates of the alkalis, and those of magnesium, calcium, zinc and copper are soluble; those of strontium, mercury (Hg'') are sparingly soluble; and those of barium, manganese, bismuth, mercury (Hg'), silver and lead are insoluble in water. Alkali chromates or dichromates are precipitated as normal chromates (in some cases as dichromates) (Preis and Rayman, *B.*, 1880, **13**, 340) by solutions of silver, lead, mercury (Hg') and barium salts. Silver chromate is dark red, soluble in nitric acid and ammonium hydroxide (§**59**, 6*h*); lead chromate is yellow, transposed with difficulty by nitric acid (Duvillier, *A. Ch.*, 1873, (4), **30**, 212), insoluble in acetic acid (§**57**, 6*h*); barium chromate, yellow, is soluble in hydrochloric and nitric acids, sparingly soluble in chromic acid (§**186**, 6*h*).

7. **Ignition.**—Chromic oxide, chromic salts and chromates dissolve in beads of microcosmic salt, and of borax, before the blow-pipe, in both reducing and oxidizing flames, with a yellowish-green tint while hot, becoming emerald green when cold. By ignition on charcoal the carbon deoxidizes chromic anhydride, CrO_3, free or combined, and a green mass, Cr_2O_3, is left. When chromium compounds are fused with an alkali carbonate, and a nitrite, nitrate, chlorate, bromate or iodate, an alkali chromate is formed, soluble in water (distinction from **Al** and **Fe**).

8. **Detection.**—If present as chromate (solution red or yellow), it is

reduced by **HCl** and alcohol or by H_2S. Precipitated with Fe''' and **Al**, after the removal of the metals of the first and second groups, by NH_4OH in presence of NH_4Cl. Boiling with **KOH** separates the **Al** and leaves the **Cr** and the **Fe**, as hydroxides. The precipitate is fused on a platinum foil with Na_2CO_3 and KNO_3 which oxidizes the **Cr** to an alkali chromate, soluble in water (separation from the **Fe**). The **Cr** is identified after acidulation with $HC_2H_3O_2$ by the formation of the yellow lead chromate, using $Pb(C_2H_3O_2)_2$. These metals may also be separated by the methods given in **10**.

9. **Estimation.**—Chromium is usually estimated gravimetrically (*1*) as the oxide. It is brought into this form either by precipitation as a hydroxide (*6a*) and ignition or, in many cases, by simple ignition (*4*). (*2*) As chromate, it may be precipitated with barium chloride, dried and weighed as such; or in acetic acid solution it may be precipitated as $PbCrO_4$ by $Pb(C_2H_3O_2)_2$, dried and weighed. Volumetrically, as a chromate (if present as chromic salt it may be oxidized to a chromate). (*3*) By titration with a standard solution of ferrous sulphate. (*4*) By liberation of iodine from hydriodic acid (*6g*) and measuring the amount of iodine liberated with standard sodium thiosulphate solution.

10. **Oxidation.**—Chromous compounds are very strong reducing agents, changing $HgCl_2$ to $HgCl$, $CuSO_4$ to $Cu°$, $SnCl_2$ to $Sn°$, etc. Chromic compounds are oxidized to chromates by chlorates (Giacomelli, *L'Orosi*, 1895, **18**, 48; Storer, *Am. S.*, 1869, **98**, 190) (*6f*), Na_2O_2, MnO_2 (Marchal and Wiernick, *Z. angew.*, 1891, 511), and PbO_2 in acid solution; in alkaline mixture, by reducing PbO_2 to PbO, Ag_2O to $Ag°$, Hg_2O and HgO to $Hg°$, CuO to Cu_2O, $KMnO_4$ and K_2MnO_4 to MnO_2 (Donath and Jeller, *C. C.*, 1887, 151); by **Cl**, **Br**, and **I**, forming the corresponding halide; and by H_2O_2* (Baumann, *Z. angew.*, 1891, 139).

The halogens in alkaline solution may be used to separate chromium from iron and aluminum. The halogens react with the alkali and oxidize the chromium to chromate according with the following reactions:

$$2NaOH + Cl_2 = NaCl + NaClO + H_2O$$
$$2NaCrO_2 + 3NaClO + NaOH = 2Na_2CrO_4 + 3NaCl + H_2O.$$

The ferric hydroxide is not acted upon, while the aluminum hydroxide dissolves in the fixed alkali and may be separated from the chromium by the addition of ammonium chloride and warming. Na_2O_2 or H_2O_2 in alkaline solution produce a similar reaction.

$$2NaCrO_2 + 3Na_2O_2 + 2H_2O = 2Na_2CrO_4 + 4NaOH,$$

the separation of iron and aluminum being effected by the method already given.

*The use of H_2O_2 in alkaline solution is proposed by Riggs (*Am. S.*, 1894, **148**, 409) in the separation of **Al**, **Fe** and **Cr**. 100 cc. water, 10 cc. H_2O_2, and one gram of **NaOH** are added to the freshly precipitated hydroxides and digested until effervescence ceases. Filter off the precipitate of ferric hydroxide, acidify the filtrate with acetic acid and precipitate the aluminum with ammonium hydroxide. The chromium if present will be in the filtrate as sodium chromate.

A chromate is also formed when chromium compounds are fused with an alkali carbonate and an oxidizing agent (7).

For this purpose sodium carbonate and potassium nitrate or sodium peroxide are frequently used. The following reactions take place:

$$2Cr(OH)_3 + 2Na_2CO_3 + 3KNO_3 = 2Na_2CrO_4 + 3KNO_2 + 2CO_2 + 3H_2O$$
$$2Cr(OH)_3 + 3Na_2O_2 = 2Na_2CrO_4 + 2NaOH + 2H_2O.$$

Ferric hydroxide is not acted upon while aluminium hydroxide is converted into aluminate.

$$2Al(OH)_3 + Na_2CO_3 = 2NaAlO_2 + CO_2 + 3H_2O.$$

On dissolving the fused mass in water, the three metals may be separated by the method already given.

Chromic oxide (not ignited) or chromic chloride at 440° in a current of chlorine become CrO_2Cl_2 (Moissan, *Bl.*, 1880, (2), **34**, 70). Chromic acid and chromates are reduced to chromic compounds by $H_2C_2O_4$ (Werner, *J. C.*, 1888, **53**, 602), $K_4Fe(CN)_6$, KCNS, H_2S, $(NH_4)_2S$, $Na_2S_2O_3$, SO_2, H_2O_2, etc. Of most common occurrence in qualitative analysis is the action of hydrosulphuric acid and alkali sulphides; at first sulphur is liberated, a part of which may be oxidized to sulphurous and sulphuric acids (Parsons, *C. N.*, 1878, **38**, 228).

$$2K_2Cr_2O_7 + 16HCl + 6H_2S = 4CrCl_3 + 4KCl + 3S_2 + 14H_2O$$
$$12H_2CrO_4 + 3S_2 = 4Cr_2O_2CrO_4 + 6SO_2 + 12H_2O$$
$$2H_2CrO_4 + 3SO_2 = Cr_2(SO_4)_3 + 2H_2O$$

While H_2O_2 in alkaline solution oxidizes Cr''' to Cr^{VI}, in acid solution the reverse action takes place: $2H_2CrO_4 + 3H_2SO_4 + 3H_2O_2 = Cr_2(SO_4)_3 + 3O_2 + 8H_2O$ (Baumann, l. c.). With chromate in acid solution, the H_2O_2 *at first* gives a deep blue solution (probably of the very unstable perchromic acid, $HCrO_4$), followed by the reduction to a chromic salt. The blue color gives a very delicate test for chromium. The test is rendered more delicate by the addition of a few c.c. of ether and shaking. The ether dissolves the blue compound and forms a blue layer on standing. One part of chromic acid in 40,000 parts of water can be detected by this reaction. Vanadic acid interferes with the delicacy (Reichard, *Z.*, **40**, 577).

§126. Iron. (Ferrum). Fe = 55.84. Usual valence two and three.

1. **Properties.**—*Specific gravity*, variable, depending upon the purity and methods of preparation. 7.85 at 16° (Caron, *C. r.*, 1870, **70**, 1263), 8.139 (Chandler-Roberts, *C. N.*, 1875, **31**, 137). *Melting point*, cast iron, 1130° to 1375°; steel, 1375 to <1530°; pure iron, 1530° (*Cir. B. S.*, **35**, 1915). Pure iron is silver-white, capable of taking a remarkably fine polish; it is among the most ductile of metals, in this property being approached by nickel and cobalt (§**73**, 1); it is the hardest of the ductile metals (Calvert and Johnson, *Dingl.*, 1859, **152**, 129), and in tenacity it is surpassed only by cobalt and nickel (§**132**, 1). It softens at a red heat and may be welded at a white heat. Finely divided iron burns in the air when ignited; that made by reduction in hydrogen may ignite spontaneously when exposed to the air. When pure iron is heated, or cooled through certain ranges of temperature, polymorphic changes occur, which are

accompanied by an absorption (on heating) or an evolution (on cooling) of heat, and changes in the physical properties of the iron; these polymorphic modifications are called *Alpha, Beta* and *Gamma* iron, respectively.

Alpha iron is stable in all ranges of temperature up to 768° C. ($\mathbf{Ac_2}$) ; * at 768° C. the change *Alpha* $\rightleftarrows$ *Beta* occurs; *Beta* iron is stable between 768° C. and 909° C. ($\mathbf{Ac_3}$) ; * at 909° C. the change *Beta* $\rightarrow$ *Gamma* takes place (Burgess and Crowe, Reprint, 213, *Bul. B. S.*, **10**, 1913). *Gamma iron* is capable of dissolving, and retaining in solid solution, carbon as iron carbide ($\mathbf{Fe_3C}$) ; the presence of $\mathbf{Fe_3C}$ in solid solution, however, progressively lowers the temperature of the $\mathbf{A_3}$ * point, at which the change *Gamma* $\rightarrow$ *Beta* occurs, and causes the appearance of a third point ($\mathbf{A_1}$) * at $\pm$ 700° C., the temperature of which is unaffected by varying percentages of carbon. Because of the progressive lowering of the temperature at which the *Gamma* $\rightarrow$ *Beta* ($\mathbf{Ar_3}$) * change takes place by increasing percentages of carbon, the ($\mathbf{A_3}$) * point merges into the ($\mathbf{A_2}$) * point at $\pm$768° C., and $\pm$0.33% C. At this temperature and concentration, and between it and $\pm$700° C. ($\mathbf{A_1}$) * *Gamma* iron probably passes directly into the *alpha* modification, with a continued concentration of carbon in the solid solution still remaining, until the $\mathbf{Ar_{3\text{-}2}}$ * point and $\mathbf{Ar_1}$ * point coincide ($\mathbf{Ar_{1\text{-}2\text{-}3}}$). *

This point ($\pm$700° C., and $\pm$0.835% C.) marks the lowest temperature at which carbon (as $\mathbf{Fe_3C}$) will remain in solid solution; if the temperature falls below Ar_1.* Carbon separates from the solid solution as $\mathbf{Fe_3C}$ (cementite) and at the same instant the *Gamma* iron, which up to that moment had acted as a solvent for the carbon is transformed to *Alpha* iron, simultaneously with the precipitation of the cementite, forming that interstratified conglomerate of *Alpha* ferrite, and cementite, known as *Pearlite* (the eutectoid).

Above $\pm$ 700° C. the solubility of $\mathbf{Fe_3C}$ in *Gamma* iron increases with the temperature, reaching a maximum at a concentration of about 1.7% carbon and a temperature of 1130° C. Hence all slowly cooled iron-carbon alloys containing less than the eutectoid percentage of carbon (<0.835% C.: hypo-eutectoid steels) will consist of structurally free *Alpha Ferrite* (pure iron) and *Pearlite*; those with more than the eutectoid percentage of carbon (between 0.835% C. and 1.7% C.; hyper-eutectoid steels) will consist of structurally free *Cementite* ($\mathbf{Fe_3C}$) and *Pearlite*; those of eutectoid composition (0.835% C.; eutectoid steel), will consist of *Pearlite* only. When such steels, provided the carbon content lies between $\pm$0.25% and 1.75%, are heated to a temperature higher than $\mathbf{Ac_3}$ * ($\mathbf{Ac^{cm}}$ * in the case of hyper-eutectoid steels) and then suddenly cooled (*e.g.*, by quenching in water), the changes which would normally occur on slow cooling through $\mathbf{Ar_3}$, $\mathbf{Ar_2}$, $\mathbf{Ar_1}$ * are partially suppressed; the steel becomes hard and brittle, the carbon being retained in solid solution. This process is called "*hardening.*" The hardened steel may be "*tempered*" by reheating to temperatures *lower than* $\mathbf{Ac_1}$* ($\pm$ 700° C.) which causes certain structural changes to take place leading to the formation of a series of transition products, the general effect of which is to soften the steel somewhat and lessen its brittleness to the extent desired.

2. **Occurrence.**—Iron is rarely found native except in meteorites; the iron minerals used as ores are hematite ($\mathbf{Fe_2O_3}$), limonite ($\mathbf{2Fe(OH)_3.Fe_2O_3}$), magnetite ($\mathbf{Fe_3O_4}$) ; to a less extent, siderite ($\mathbf{FeCO_3}$), clay iron stone ($\mathbf{FeCO_3}$ with clay) black band ($\mathbf{FeCO_3}$ with bituminous matter); it also occurs as pyrite ($\mathbf{FeS_2}$), marcasite ($\mathbf{FeS_2}$), pyrrhotite ($\mathbf{Fe_nS_{n+1}}$) and widely distributed in many other minerals and rocks.

3. **Preparation.**—Pure iron is not usually found in the market, although some of the commercial products approach it very closely.

Pig iron is produced by smelting iron ore mixed with coke and limestone in blast furnaces; the resulting product is subjected to remelting processes (product, gray and malleable iron castings), or to conversion processes (products, Bessemer steel; open-hearth steel, acid and basic; wrought iron); pure iron may be made by electrolysis, and by heating its purified salts with hydrogen.

4. **Oxides and Hydroxides.**—*Ferrous oxide*, $\mathbf{FeO}$, is made from $\mathbf{Fe_2O_3}$ by heating it to 300° in an atmosphere of hydrogen; also by heating $\mathbf{FeC_2O_4}$ to 160°,

* $Ar_{1\text{-}2\text{-}3}$ is derived from Arrêt (a halt, or pause) and refroidissement (cooling); hence, a halt in cooling at certain critical temperatures. Ar_3 = 898° C.; Ar_2 = 768° C.; Ar_1 = $\pm$700° C. $Ac_{1\text{-}2\text{-}3}$ (c = chauffant, heating) refers to corresponding points during heating. Ac_3 is slightly higher (909° C.) than Ar_3. Acem or Arem refers to temperatures at which Cementite dissolves in, or is precipitated from *Gamma* iron during heating or cooling.

air being excluded. It takes fire spontaneously in the air, oxidizing to Fe_2O_3. *Ferrous hydroxide*, $Fe(OH)_2$, is formed by precipitating ferrous salts with KOH or NaOH, perfectly white when pure, but usually green from partial oxidation. *Ferric oxide*, Fe_2O_3, is formed by heating FeO, $Fe(OH)_2$, or any ferrous salt consisting of a volatile or organic acid in the air; more rapidly by heating $Fe(OH)_3$, $Fe(NO_3)_3$, or $Fe_2(SO_4)_3$. Ferric hydroxide is formed by precipitating cold dilute ferric salts with alkalis or alkali carbonates, and drying at 100°. If KOH or NaOH is used, the precipitate requires longer washing than when NH_4OH is employed. By increasing the temperature and concentration of the solutions, the following definite compounds may be formed: $FeO(OH)$, $Fe_2O(OH)_4$, $Fe_4O_5(OH)_2$, $Fe_4O_3(OH)_6$, $Fe_3O_2(OH)_5$. Fe_3O_4 is slowly formed by heating FeO or Fe_2O_3 to a white heat. Its corresponding hydroxide may be made by precipitation: $FeCl_2 + 2FeCl_3 + 8NH_4OH = Fe_3(OH)_8 + 8NH_4Cl$. $Fe_3(OH)_8$ when heated to 90° forms Fe_3O_4. The black color and magnetic properties show that it is a chemical *salt* and not a mechanical mixture of FeO and Fe_2O_3. Fe‴ acts as an acid towards the Fe″; this oxide, Fe_3O_4, or $FeFe_2O_4$, may be called ferrous ferrite. Other ferrites have been formed, *e. g.*, calcium ferrite, $CaFe_2O_4$; $MgFe_2O_4$ and $BaFe_2O_4$ (List, *B.*, 1878, **11**, 1512); zinc ferrite, $ZnFe_2O_4$. Compare potassium aluminate, $KAlO_2$ (§124, 6a), and potassium chromite, $KCrO_2$ (§125, 6a). *Ferric acid*, H_2FeO_4, and its anhydride, FeO_3, have not been isolated. *Potassium ferrate*, K_2FeO_4, is made (*1*) by electrolysis; (*2*) by heating iron-filings, FeO or Fe_2O_3, to a red heat with KNO_3; (*3*) by heating $Fe(OH)_3$ with potassium peroxide K_2O_2; (*4*) by passing Cl or Br into a solution of 5 parts of KOH in 8 parts of water in which $Fe(OH)_3$ is suspended; the temperature should be not above 50°. It has a purple color; is a strong oxidizing agent. It slowly decomposes on standing: $4K_2FeO_4 + 10H_2O = 8KOH + 4Fe(OH)_3 + 3O_2$. With barium salts it precipitates a stable barium ferrate, $BaFeO_4$.

5. Solubilities.—*a. Metal.* Iron dissolves, in hydrochloric acid and in dilute sulphuric acid, to ferrous salts, with liberation of hydrogen (*a*); concentrated cold H_2SO_4 has no action, but if hot, SO_2 is evolved and a ferric salt formed (*b*); in moderately dilute nitric acid, with heat, to ferric nitrate, liberating chiefly nitric oxide (*c*); in cold dilute nitric acid, forming ferrous nitrate with production of ammonium nitrate (*d*), of nitrous oxide (*e*), or of hydrogen *f*) (Langlois, *A. Ch.*, 1856, [3], **48**, 502).

(*a*) $Fe + H_2SO_4 = FeSO_4 + H_2$

(*b*) $2Fe + 6H_2SO_4 = Fe_2(SO_4)_3 + 3SO_2 + 6H_2O$

(*c*) $Fe + 4HNO_3 = Fe(NO_3)_3 + NO + 2H_2O$

(*d*) $4Fe + 10HNO_3 = 4Fe(NO_3)_2 + NH_4NO_3 + 3H_2O$

(*e*) $4Fe + 10HNO_3 = 4Fe(NO_3)_2 + N_2O + 5H_2O$

(*f*) $Fe + 2HNO_3 = Fe(NO_3)_2 + H_2$

In dissolving the iron of commerce in hydrochloric acid, the carbon which it always contains, so far as combined in the carbide of iron, will pass off in gaseous hydrocarbons (Campbell, *Am.*, 1896, **18**, 836), and so far as uncombined will remain undissolved, as graphitic carbon. The metal is attacked by moist air, forming chiefly $2Fe_2O_3.3H_2O$, iron rust. When hot iron is hammered, scale oxide, $Fe_3O_4.6FeO$, is formed. Cold concentrated HNO_3 or the action of the electric current forms passive iron. (Byers and Langdon, *J. Am. Soc.*, **35**, 759, 1913) (Byers, *Ibid.*, **30**, 1718, 1908).

b.—Oxides and hydroxides.—*Ferrous oxide* and *hydroxide* unite with acids with rapid increase in temperature, forming ferrous salts, always mixed with more or less ferric salts. The ferrous salts are much more readily prepared by the action of dilute acids upon the metal, or upon $FeCO_3$ or FeS. Fe_3O_4, treated with an insufficient amount of HCl, forms $FeCl_2$ and Fe_2O_3; treated with HCl sufficient for complete solution, a mixture of $FeCl_2$ and $FeCl_3$ is obtained, which, when treated with excess of ammonium hydroxide and dried at 100° again exhibits the magnetic properties of the original. *Ferric oxide*, Fe_2O_3, dissolves in acids, quite slowly if the temperature of preparation of the oxide has been high. Mitscherlich (*J. pr.*, 1860, **81**, 110) recommends warm digestion with ten parts of a mixture of sulphuric acid and water (8:3). If the oxide be

heated with alkalis or alkali carbonates, it then dissolves much more readily in acids. *Ferric hydroxide*, $Fe(OH)_3$, is insoluble in water (for a soluble colloidal ferric hydroxide, see Sabanejeff, *C. C.*, 1891, i, 11), readily soluble in acids to ferric salts. Freshly precipitated ferric hydroxide readily dissolves in ferric chloride and in chromium chloride, not in aluminum chloride. A solution of ferric hydroxide in ferric chloride is soluble in water after evaporation to dryness if not more than ten parts of Fe_2O_3 are present to one of the $FeCl_3$ (Bechamp, *A. Ch.*, 1859, (3), **56**, 306).

c.—*Salts.*—*Ferrous* salts, in crystals and in solution, have a light green color. Solutions of the salts have a slight acid reaction toward litmus. The sulphate $FeSO_4.7H_2O$, is efflorescent; the chloride, bromide, iodide, and citrate are *deliquescent*. Solutions of all ferrous salts are unstable, gradually changing to basic ferric salts, more or less insoluble in water. The carbonate, hydroxide, phosphate, borate, oxalate, cyanide, ferrocyanide, ferricyanide, tartrate, and tannate are insoluble in water. *Ferric* salts in solution have a brownish-yellow color, redden litmus and color the skin yellow. The chloride, bromide, nitrate, and sulphate are *deliquescent*. The ferrocyanide, tannate, borate, phosphate, basic acetate, and sulphite are insoluble in water; the sulphate is soluble in alcohol (separation from ferrous sulphate). Ferric chloride is soluble in ether saturated with hydrochloric acid, separation from aluminum (Gooch and Havens, *Am. S.*, 1896, **152**, 416). Solutions of ferric salts, when boiled, frequently precipitate a large portion of the iron as basic salt, especially if other soluble salts are present (Fritsche, *Z. angew.*, 1888, 227; Pickering, *J. C.*, 1880, **37**, 807) (§**70**, 5*d* footnote).

6. **Reactions.** *a*.—The **alkali hydroxides** precipitate *ferrous hydroxide*, $Fe(OH)_2$, white if pure, but seldom obtained sufficiently free from ferric hydroxide to be clear white, and quickly changing, in the air, to ferroso-ferric hydroxide, of a dirty-green to black color, then to ferric hydroxide (4), of a reddish-brown color. The fixed alkalis adhere to this precipitate. **Ammonium chloride** or sulphate, sugar, and many organic acids, to a slight extent, dissolve the ferrous hydroxide or prevent its formation (§§**116** and **117**). The soluble **carbonates** precipitate, from purely ferrous solutions, *ferrous carbonate*, $FeCO_3$, white if pure, but soon changing, in the air, to the reddish-brown ferric hydroxide.

Solutions of ferric salts are precipitated by the **alkali hydroxides** and **carbonates** as *ferric hydroxide*, $Fe(OH)_3$, variable to $Fe_2O_3.H_2O$ — $FeO(OH)$ — reddish-brown insoluble in excess of the reagents (distinction from aluminum and chromium which are soluble in excess of the fixed alkali hydroxides and from cobalt, nickel and zinc which are soluble in ammonium hydroxide). Salts of the fixed alkalis adhere to this precipitate with great tenacity and the precipitate obtained from the use of the fixed alkali carbonates invariably contains traces of a carbonate. Freshly precipitated **barium carbonate** completely precipitates ferric salts in the cold as ferric

hydroxide (separation of ferric iron, with aluminum and chromium, from ferrous iron, cobalt, nickel, manganese, and zinc; $2FeCl_3 + 3BaCO_3 + 3H_2O = 2Fe(OH)_3 + 3BaCl_2 + 3CO_2$). The mixture should be allowed to stand several hours (chromium precipitates more slowly than aluminum or iron), and, sulphates must be absent, as freshly precipitated barium carbonate reacts with solutions of the sulphates of the fourth group; *e. g.*, $NiSO_4 + BaCO_3 = NiCO_3 + BaSO_4$. The reaction takes place most readily if the metals be present as chlorides. If the precipitate obtained be treated with an excess of dilute sulphuric acid the ferric hydroxide dissolves, leaving the excess of barium as the insoluble sulphate. Freshly precipitated carbonates of **Ca**, **Mg**, **Mn**, **Zn**, and **Cu** react similar to the barium carbonate.

b.—**Oxalic acid** and soluble **oxalates** precipitate from solutions of ferrous salts, ferrous oxalate, FeC_2O_4, yellowish-white, crystalline, sparingly soluble in hot water, soluble in **HCl**, HNO_3 and H_2SO_4; ferric salts are not precipitated by oxalates except as reduction to ferrous oxalate takes place.

The acetates, as $NaC_2H_3O_2$, form in solutions of ferric salts a dull red * solution of ferric acetate, $Fe(C_2H_3O_2)_3$, which upon boiling is decomposed and precipitated as basic ferric acetate of variable composition (separation of iron and aluminum from phosphoric acid (*d*), chromium, and the metals of the fourth group). The red colored ferric acetate solution is not decolored by mercuric chloride (distinction from $Fe(CNS)_3$). The basic precipitates are soluble in **HCl**, HNO_3 and H_2SO_4 and are transposed by alkali hydroxides.

Tannic acid precipitates concentrated solutions of ferrous salts; ferric salts are precipitated as blue-black ferric tannate (*the basis of common ink*), insoluble in water or acetic acid, very soluble in excess of tannic acid. Ferric salts are completely precipitated by **ammonium succinate** from hot solutions (Young, *J. C.*, 1880, **37**, 674). Both ferrous and ferric salts (not nitrates) slightly acid are completely precipitated by a solution of **nitroso B. naphthol** (separation from aluminum and chromium) (Knorre, *B.*, 1887, **20**, 283; Menicke, *Z. angew.*, 1888, 5). If the Fe''' be in excess of the PO_4 the phosphate will all be precipitated. Hydrochloric acid should be absent, *i. e.*, excess of $NaC_2H_3O_2$ should be added (Knorre, *Z. angew.*, 1893, 267).

Potassium cyanide gives with solutions of ferrous salts a yellowish-red precipitate, which dissolves in excess of the reagent to potassium ferrocyanide, $K_4Fe(CN)_6$; with solutions of ferric salts, ferric hydroxide is precipitated with evolution of hydrocyanic acid (equation (*a*), page 156).

Potassium ferrocyanide precipitates ferrous salts as *potassium ferrous ferrocyanide* (*b*), $K_2FeFe(CN)_6$, (Everitt's salt), bluish-white, insoluble in

* Meconic acid and formic acid form red solutions with ferric salts; benzoic acid gives a flesh colored precipitate; phenol, creosote, saligenin, and other hydroxy aromatic derivatives give a blue to violet color. Morphine gives a blue color. The following is recommended as a very satisfactory test for a trace of iron in copper sulphate. Dissolve one gram of the $CuSO_4$ in five cc. of water, add five cc. of a ten per cent. etherial solution of salicylic acid. If the layer of contact assumes a violet color iron is present (Grigge, *Z.*, 1895, **34**, 450).

acids, transposed by alkalis (*c*). This is converted into Prussian blue (see below), gradually by exposure to the air, immediately by oxidizing agents (*d*). With ferric salts, *ferric ferrocyanide* (*e*), $Fe_4(Fe(CN)_6)_3$, Prussian blue, is formed, insoluble in acids, decomposed by alkalis (*f*). If the reagent be added in strong excess the precipitate is partially dissolved to a blue liquid. Strong acids should not be present as they color the reagent blue. In neutral solutions diluted to one in 500,000 the iron may be detected (Wagner, *Z.*, 1881, **20**, 350). The ferrocyanides are transposed by **KOH** and decomposed by fusion with $NaNO_3$ and Na_2CO_3, the iron being obtained as Fe_2O_3 (Koningh, *Z. angew.*, 1898, 463). **Potassium ferricyanide** precipitates from dilute solutions of ferrous salts *ferrous ferricyanide* (*g*), $Fe_3(Fe(CN)_6)_2$ (Turnbull's blue), dark blue, insoluble in acids, transposed by alkali hydroxides (*h*): with ferric salts no precipitate is obtained, but the solution is colored brown or green (*i*). This is a very important reagent for the detection of the presence of even traces of ferrous salts in the presence of ferric salts. As iron is so readily oxidized or reduced by various reagents the original solution should always be tested. The solutions should also be sufficiently diluted to allow the detection of the precipitate of the *ferrous ferricyanide* in the presence of the dark colored liquid due to the presence of ferric salts. If no precipitate be obtained (indicating absence of ferrous iron) a drop of stannous chloride or some other strong reducing agent constitutes a delicate test for ferric salts and reconfirms the previous absence of ferrous salts. **Potassium thiocyanate** gives no reaction with ferrous salts; with ferric salts the *blood red ferric thiocyanate*, $Fe(CNS)_3$ (solution),* is formed (*j*). This constitutes an exceedingly delicate test for iron in the ferric condition (the original solution should always be tested). According to Wagner (*Z.*, 1881, **20**, 350) one part of iron, as ferric salt, may be detected in 1,600,000 parts of water. The red salt of ferric thiocyanate is freely soluble in water, alcohol, and ether; it is extracted by ether from aqueous solutions and thus concentrated, increasing the delicacy of the test (Natanson, *A.*, 1864, **130**, 246). The red color of the liquid is destroyed by mercuric chloride (*k*), also by phosphates, borates, acetates, oxalates, tartrates, racemates, malates, citrates, succinates, and the acids of these salts. Nitric and chloric acids give red color with potassium thiocyanate, removed by heat.

* The quantity of non-dissociated $Fe(CNS)_3$, to which the color is due, is increased by an excess of either of the products of the dissociation. The test for iron is therefore more delicate if considerable **KCNS** is added. The decoloration by $HgCl_2$ is due to the breaking up of the $Fe(CNS)_3$ to form $Hg(CNS)_2$ which is even less dissociated in water solution than $HgCl_2$.

(*a*) $FeCl_3 + 3KCN + 3H_2O = Fe(OH)_3 + 3KCl + 3HCN$
(*b*) $FeSO_4 + K_4Fe(CN)_6 = K_2FeFe(CN)_6 + K_2SO_4$
(*c*) $K_2FeFe(CN)_6 + 2KOH = Fe(OH)_2 + K_4Fe(CN)_6$
(*d*) $4K_2FeFe(CN)_6 + O_2 + 4HCl = Fe_4(Fe(CN)_6)_3 + K_4Fe(CN)_6 + 4KCl + 2H_2O$
(*e*) $4FeCl_3 + 3K_4Fe(CN)_6 = Fe_4(Fe(CN)_6)_3 + 12KCl$
(*f*) $Fe_4(Fe(CN)_6)_3 + 12KOH = 4Fe(OH)_3 + 3K_4Fe(CN)_6$
(*g*) $3FeSO_4 + 2K_3Fe(CN)_6 = Fe_3(Fe(CN)_6)_2 + 3K_2SO_4$
(*h*) $Fe_3(Fe(CN)_6)_2 + 6KOH = 3Fe(OH)_2 + 2K_3Fe(CN)_6$
(*i*) $FeCl_3 + K_4Fe(CN)_6 = FeFe(CN)_6 + 3KCl$
(*j*) $FeCl_3 + 3KCNS = Fe(CNS)_3 + 3KCl$
(*k*) $2Fe(CNS)_3 + 3HgCl_2 = 3Hg(CNS)_2 + 2FeCl_3$

c.—**Nitric acid** readily oxidizes all ferrous salts to ferric salts, the reaction being hastened by the aid of heat. As the iron is reduced to the ferrous condition in the precipitation of the metals of the second group with hydrosulphuric acid, the oxidation with nitric acid is necessary to insure the precipitation of all the iron as hydroxide in the third group (6*a* and §117).

d.—**Hypophosphorous acid** reduces ferric salts to ferrous salts. From solutions of *ferrous salts*, **alkali phosphates**, as Na_2HPO_4, precipitate secondary ferrous phosphate. $FeHPO_4$, mixed with the tertiary salt, $Fe_3(PO_4)_2$, white to bluish white, soluble in mineral acids. By the addition of an alkali acetate, the precipitate consists of the tertiary phosphate alone: $3FeSO_4 + 2Na_2HPO_4 + 2NaC_2H_3O_2 = Fe_3(PO_4)_2 + 3Na_2SO_4 + 2HC_2H_3O_2$. *Ferric salts* are precipitated as ferric phosphate, $FePO_4$, scarcely at all soluble in acetic acid, but readily soluble in hydrochloric, nitric and sulphuric acids.* Hence ferric iron in mineral acid solution is precipitated by phosphoric acid with co-operation of alkali acetates: $FeCl_3 + H_3PO_4 + 3NaC_2H_3O_2 = FePO_4 + 3NaCl + 3HC_2H_3O_2$. If metals of the fourth group and the alkaline earths be present with phosphoric acid they are precipitated with the third group metals by ammonium hydroxide in the usual course of analysis (§146 and *ff*.); phosphates of **Co**, **Ni**, and **Zn** being redissolved by the excess of ammonium hydroxide. To prevent this general precipitation with the metals of the third group, when phosphates are present, the acid solution (after removal of the second group by hydro-

* Equilibrium requires that a weak acid, as phosphoric, be present for the most part as the non-dissociated molecule. But $FePO_4$, as any neutral salt, is dissociated, so far as it dissolves in water, into its ions, as is also the strong hydrochloric acid. Bringing these together will result in the union of the **H** ion of the acid and the PO_4 ion to non-dissociated H_3PO_4, thus maintaining the equilibrium for H_3PO_4, but disturbing that between solid and dissolved $FePO_4$, which requires a certain concentration of PO_4 ions. To restore the latter more $FePO_4$ dissolves, only to react with the **H** ions as before, and this process continues until the **H** ions of the hydrochloric acid are reduced to such small quantity as to be in equilibrium with the PO_4 ions or, if the **HCl** is in excess, until the $FePO_4$ is entirely dissolved. This process takes place whenever a strong acid dissolves the salt of a weak one. It is analogous to the solution of a base in an acid, forming non-dissociated water.

gen sulphide and the expulsion of the gas by boiling) is treated with an excess of sodium acetate. Acetic acid is liberated by the mineral acid and phosphates of iron, aluminum and chromium are precipitated. If no more phosphoric acid remains in the solution, the remainder of the iron, aluminum and chromium may be precipitated by means of ammonia. If on the other hand the solution contains phosphoric acid it must be removed. For this purpose ferric chloride is added drop by drop, until a red color indicates complete precipitation of the phosphate and formation of ferric acetate. The mixture is then boiled and filtered hot. All of the phosphoric acid present is thus precipitated and separated from the metals of the remaining groups. Care should be taken to avoid an excess of the ferric chloride as the ferric phosphate is somewhat soluble in ferric acetate solution. The **alkali hydroxides** transpose ferric phosphate (freshly precipitated), forming *ferric hydroxide* and *alkali phosphate*. The transposition is not complete in the cold. With fixed alkali hydroxide aluminum phosphate is dissolved, thus effecting a separation from chromium and iron. Ferric phosphate warmed with ammonium sulphide forms ferrous sulphide, ammonium phosphate and sulphur: $4FePO_4 + 6(NH_4)_2S = 4FeS + 4(NH_4)_3PO_4 + S_2$.

e.—**Hydrosulphuric acid** is without action upon ferrous salts in acid or neutral solutions, except a slight precipitate is formed with neutral ferrous acetate. **Alkali sulphides** and H_2S in alkaline mixture, form *ferrous sulphide*, **FeS**, black, insoluble in excess of the reagent, readily soluble in dilute acids with evolution of hydrogen sulphide. The moist precipitate is slowly converted, in the air, to ferrous sulphate and finally to basic ferric sulphate, $Fe_2O(SO_4)_2$. Ferric salts are reduced to ferrous salts with liberation of sulphur by H_2S (*1*), or soluble sulphides, the latter at once reacting to precipitate ferrous sulphide (*2*):

(*1*) $4FeCl_3 + 2H_2S = 4FeCl_2 + 4HCl + S_2$

(*2*) $4FeCl_3 + 6(NH_4)_2S = 4FeS + 12NH_4Cl + S_2$

After the removal of the metals of the second group by H_2S, the iron present will always be in the ferrous condition (it will therefore be necessary to test the original solution to find the condition of the iron at the beginning of the analysis). The excess of H_2S should be removed by boiling and the iron oxidized by carefully adding nitric acid drop by drop and boiling until the solution assumes a pale straw color (6*b*). If this be done the iron will be completely precipitated in the third group by the ammonium hydroxide (6*a*).

Ferrous sulphite is but little soluble in pure water, easily soluble in excess of **sulphurous acid**, to a colorless solution. The moist salt oxidizes rapidly on exposure to the air (Fordos and Gelis, *J. Pharm.*, 1843, (3), **4**, 333). *Ferric sulphite* is only known as a red solution formed by the action of SO_2 upon freshly precipitated $Fe(OH)_3$, rapidly reduced to the ferrous condition accord-

ing to the following equation: $Fe_2(SO_3)_3 = FeSO_3 + FeS_2O_6$ (Gelis, *C. C.*, 1862, 896). *Ferrous thiosulphate*, FeS_2O_3, is formed, together with some FeS and $FeSO_3$, by the action of SO_2 upon Fe° (Fordos and Gelis, *l. c.*). Ferric salts are reduced by **sodium thiosulphate** to ferrous salts in neutral solutions with formation of sodium tetrathionate: $2FeCl_3 + 2Na_2S_2O_3 = 2FeCl_2 + 2NaCl + Na_2S_4O_6$ (Fordos and Gelis, *C. r.*, 1842, **15**, 920); in acid solutions sulphuric acid and sulphur are formed: $4FeCl_3 + 2Na_2S_2O_3 + 2H_2O = 4FeCl_2 + 4NaCl + 2H_2SO_4 + S_2$ (Menschutkin, 78). Ferric iron is precipitated as basic nitrate by the addition of a solution of **ammonium sulphate** to a solution of iron in HNO_3 evaporated to dryness and taken up with water (separation from aluminum) (Beilstein and Luther, *C. C.*, 1891, i, 809).

f.—Chlorides and bromides of both ferrous and ferric iron are formed but only ferrous iodide exists. Ferric salts are reduced to ferrous salts by **hydriodic acid** with liberation of iodine.

g.—Soluble **arsenites** and **arsenates** precipitate solutions of ferrous and ferric salts, forming the corresponding arsenites and arsenates. Basic ferric arsenite, $4Fe_2O_3.As_2O_3 + 5H_2O$, is formed when an excess of ferric hydroxide is added to arsenous acid. It is insoluble in acetic acid. It is formed when moist ferric hydroxide is given as an antidote in case of arsenic poisoning (§69, 6*l* and 6′*e*; D., **3**, 352).

h. Ferrous salts are rapidly oxidized to ferric salts by solutions of **chromates**, the chromium being reduced to the triad condition (9 and 10). With ferric salts potassium chromate forms a reddish-brown precipitate.

i.—Zinc oxide precipitates solutions of Fe‴, Al, Cr‴ and Cu completely and Pb partially, effecting a separation of these metals from Mn, Co and Ni (Meineke, *Z. angew.*, 1888, 258).

7. **Ignition.**—The larger number of iron salts are decomposed, as solids, by heat; $FeCl_3$ vaporizes partly decomposed, at a very little above 100°. Ignition in the air changes ferrous compounds, and ignition on charcoal or by reducing flame changes ferric compounds to the magnetic oxide, which is attracted to the magnet. Ferrous oxalate ignited in absence of air gives FeO. Ferric oxide ignited in a current of hydrogen gives Fe_3O_4 from 330° to 440°, FeO from 500° to 600°, and Fe° above 600° (Moissan, *A. Ch.*, 1880, (5), **21**, 199).

In the outer **flame**, the **borax bead**, when moderately saturated with any compound of iron, acquires a reddish color while hot, fading and becoming light *yellow* when cold, or colorless, if feebly saturated. The same bead, held persistently in the *reducing* flame, becomes colorless unless strongly saturated, when it shows the pale *green* color of ferrous compounds. The reactions with **microcosmic salt** are less distinct, but similar. Cobalt, nickel, chromium and copper conceal the reaction of iron in the bead.

Ferric compounds, heated briefly in a **blue borax bead** holding a very little **cupric oxide**, leave the bead blue; ferrous compounds so treated change the blue bead to red—the color of cuprous oxide.

8. **Detection.**—After removal of the first two groups the iron (now in the ferrous condition) is oxidized by HNO_3 and then precipitated in presence of NH_4Cl with Al and Cr‴ by an excess of NH_4OH. The Al is removed by boiling with excess of KOH. If more than traces of Fe be present it is detected in presence of the $Cr(OH)_3$, by dissolving in HCl and obtaining the blood-red solution with KCNS. In case Cr be present in great excess the $Cr(OH)_3$ and $Fe(OH)_3$ are fused on a platinum foil with

Na_2CO_3 and KNO_3, oxidizing the Cr to a chromate soluble in water. After filtering, the precipitate of Fe_2O_3 is dissolved in HCl and tested with KCNS. The original solution must be tested to determine whether the iron was present in the ferrous or ferric condition. A portion of the original solution acidified with HCl gives blood red color with KCNS if Fe‴ is present, no color for the Fe″. Another portion gives a blue precipitate with $K_3Fe(CN)_6$ if Fe″ is present, only a brown or green color for the Fe‴(6b). Ferrous iron, in the presence of ferric, may be detected as follows: To a small portion of the solution to be tested an equal volume of concentrated sulphuric acid is added without mixing. After cooling the solution a a crystal of potassium nitrate is added. On shaking the test tube gently a red to brown color develops if ferrous iron is present. Blum, *Z.*, **44**, 10.

9. **Estimation.**—(*1*) After oxidation to Fe‴, if necessary, it is precipitated with NH_4OH, dried, ignited to a dull-red heat and weighed as Fe_2O_3. (*2*) By precipitation with nitroso-β-naphthol in slightly acid solution (Knorre, *B.*, 1887, **20**, 283). Volumetrically: (*3*) As ferrous iron, by titration with a standard solution of $KMnO_4$: $10FeSO_4 + 2KMnO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$. (*4*) By titration with a standard solution of $K_2Cr_2O_7$, using a solution of $K_3Fe(CN)_6$ as an external indicator: $6FeSO_4 + K_2Cr_2O_7 + 7H_2SO_4 = 3Fe_2(SO_4)_3 + K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O$. (*5*) As ferric iron, by titration with a standard solution of $Na_2S_2O_3$, using KCNS as an indicator: $2FeCl_3 + 2Na_2S_2O_3 = 2FeCl_2 + Na_2S_4O_6 + 2NaCl$. A few drops of a solution of $CuSO_4$ are added, which seems to hasten the reaction and gives more accurate results; or use excess of the $Na_2S_2O_3$ and titrate back with standard iodine (Crafts, *J. C.*, 1873, **26**, 1162). (*6*) The iron as ferric salt is treated with an excess of a standard $SnCl_2$ solution, the excess of the $SnCl_2$ being determined by a standard solution of iodine in potassium iodide: $2FeCl_3 + SnCl_2 = 2FeCl_2 + SnCl_4$. (*7*) Potassium iodide is added to the nearly neutral ferric chloride; the flask is stoppered and warmed to 40°. The iodine set free is titrated by standard $Na_2S_2O_3$ (very accurate for small amounts of iron). (*8*) When present in traces it is determined colorimetrically as $Fe(CNS)_3$ in etherial solution (Lunge, *Z. angew.*, 1894, 669).

10. **Oxidation.**—Metallic iron precipitates the free metals from solutions of Au, Pt, Ag, Hg, Bi, and Cu (separation from Cd).

Solutions of Fe″ are changed to Fe‴ solutions by treating with solutions of Au, Ag, Cr^{VI}, Mn^{VII}, Mn^{VI}, and H_2O_2. In presence of some dilute acid, such as H_2SO_4 or H_3PO_4 by PbO_2, Pb_3O_4, Mn_3O_4, MnO_2, Mn_2O_3, Co_2O_3, Ni_2O_3. The following acids also oxidize Fe″ to Fe‴, HNO_2, HNO_3, HClO, $HClO_2$, $HClO_3$, HSO_4 (if concentrated and hot), HBrO, $HBrO_3$ HIO_3, also Br, Cl. Br and Cl in presence of KOH changes Fe″ and Fe‴ to K_2FeO_4. Barium ferrate is the most stable of the ferrates; they are strong oxidizers, acting upon nitrites, tartrates, glycerol, alcohol, ether, ammonia, etc. (Rosell, *J. Am. Soc.*, 1895, **17**, 760).

Fe‴ is reduced to Fe″ by solutions of Sn″, Cu′, H_3PO_2, H_3PO_3, H_2S, H_2SO_3, $Na_2S_2O_3$, and HI. Also by nascent hydrogen, or by any of the metals which produce hydrogen when treated with acids, including Pb, As, Sb, Sn, Bi, Cu *, Cd, Fe, Al, Co, Ni, Zn, and Mg †.

* Carnegie, *J. C.*, 1888, **53**, 468.

† Warren, *C. N.*, 1889, **60**, 187.

§127. Table for Analysis of the Iron or Third Group (Phosphates and Oxalates being absent). See §312.

To the clear **filtrate** from the **Second Group,** in which H_2S will cause no precipitate (§80), and freed from H_2S by **boiling,** add a few drops of **Nitric Acid** and *boil* an instant (to oxidize the ferrous iron *). Immediately add **Ammonium Chloride** (§134, 5*b*; §189, 5*b*) and an excess (§135, 6*a*) of **Ammonium Hydroxide** (§116). If there is a precipitate, filter and wash.

Precipitate: $Al(OH)_3$, $Cr(OH)_3$, $Fe(OH)_3$ [$Mn(OH)_3$].

Pierce the point of the filter, and with a little water wash the precipitate into a casserole or evaporating dish. Add 5 to 10 cc. of **NaOH** and 10 to 15 cc. of H_2O_2 or add a gram or two of sodium peroxide. Boil several minutes, dilute and filter.

Residue: $Fe(OH)_3$, $Mn(OH)_3$

Dissolve in dilute H_2SO_4, adding a few drops of H_2O_2 if necessary. Divide in two parts.

(1) Add **KCNS.** Blood-red color indicates iron (§ 126, 6*b*).

(2) Boil with HNO_3 and PbO_2 or Pb_3O_4. Reddish purple solution indicates manganese.

Iron being found, to determine whether it is ferric or ferrous, or both†, in the original solution, test the latter, after acidulating with hydrochloric acid, with **KCNS** for ferricum, and with $K_3Fe(CN)_6$ for ferrosum (§ 126, 6*b*).

Study § 136, § 128, § 129, § 130, and §131.

Filtrate: Na_2CrO_4, $NaAlO_2$

Acidify with acetic acid and divide into two parts.

(1) Test for chromium. Add a few drops of lead acetate. The yellow lead chromate indicates chromium (§ 57, 6*h*).

If the original solution contains a chromate it will be yellow (normal chromate), or red (acid chromate), and will give the reactions for chromates with $Pb(C_2H_3O_2)_2$, $BaCl_2$, etc. (§ 125, 6h). If the chromium is present as a chromic salt, $Cr_2(SO_4)_3$, the solution will have a green or bluish-green color and will give the general reactions as described at § 125, 6.

Chromates should be reduced by boiling with **HCl** and C_2H_5OH before proceeding with the regular course of analysis (§ 125, 6*f*).

Study §136, §128, §129, §130, §131.

(2) Test for aluminum. Add $(NH_4)_2CO_3$ in excess and heat. A precipitate is $Al(OH)_3$.

The same result is obtained with nearly equal certainty by adding an excess of NH_4Cl to the alkaline solution § 124, 6a; § 130).

Lead and antimony give similar results if (through carelessness) they have not been removed (§ 131, 6).

Study § 136, § 128, §129. § 131, *6* and § 124, 6.

* In the filtrate from the **Second Group** iron is necessarily in the ferrous condition (126, 6*e*).

† Ferrous salts, which have been kept in the air, are never wholly free from ferric compounds.

Directions for the Analysis of the Metals of the Third Group.

§128. **Manipulation.**—Boil the filtrate from the second group (§80) to expel the H_2S and then oxidize any ferrous iron that may be present by the addition of a few drops of HNO_3, continuing the boiling to a clear straw-colored solution (§126, 6*c*):

$$3FeSO_4 + 4HNO_3 = Fe_2(SO_4)_3 + Fe(NO_3)_3 + NO + 2H_2O$$

Add to the solution about one-half its volume of NH_4Cl (5*b*, §§134 and 189) and warm and then add NH_4OH in a decided excess (§135, 6*a*):

$$MgCl_2 + NH_4Cl + NH_4OH = NH_4MgCl_3 + NH_4OH$$
$$Fe_2(SO_4)_3 + 6NH_4OH = 2Fe(OH)_3 + 3(NH_4)_2SO_4$$
$$ZnSO_4 + 4NH_4OH = (NH_4)_2ZnO_2 + (NH_4)_2SO_4 + 2H_2O$$

Heat nearly to boiling for a moment, filter, and wash with hot water. Notice that the filtrate has a strong odor of ammonium hydroxide and set aside to be tested for the metals of the succeeding groups (§138).

§129. *Notes.*—(*1*) If the H_2S is not all expelled, it becomes oxidized by the HNO_3 with deposition of a milky precipitate of sulphur (§257, 6*B*), which tends to obscure the reactions following: $6H_2S + 4HNO_3 = 3S_2 + 4NO + 8H_2O$. Also any H_2S not decomposed by the HNO_3 would cause a precipitate of the sulphides of the fourth group upon the addition of the NH_4OH: $H_2S + NiCl_2 + 2NH_4OH = NiS + 2NH_4Cl + 2H_2O$.

(*2*) Any iron that may have been present in the original solution in the ferric condition is reduced to the ferrous condition by the H_2S (§126, 6*c*): $4FeCl_3 + 2H_2S = 4FeCl_2 + S_2 + 4HCl$. The ferrous hydroxide is not completely insoluble in the ammonium salts present (§117), and hence unless the oxidation with the HNO_3 be complete, some of the iron will be found in the next group.

(*3*) If considerable iron be present the solution becomes nearly black upon addition of nitric acid, due to the combination of the nitric oxide with the ferrous iron (§241, 8*a*). Therefore the boiling, and addition of HNO_3, a drop or two at a time, must be continued until the solution assumes a bright straw color.

(*4*) If nitric acid be added in excess there is danger that Mn will be oxidized to the triad or tetrad condition then it is precipitated with iron in the third group (§134, 6*a*). The careful addition of the nitric acid (avoiding an excess) prevents this oxidation of the manganese.

(*5*) Ammonium hydroxide precipitates a portion of Mn (§134, 6*a*) and Mg (§189, 6*a*), but these hydroxides are soluble in NH_4Cl (5*c*, §§134 and 189); hence if that reagent be added in excess the Mg is not at all precipitated by the NH_4OH, but the manganese is oxidized to $Mn(OH)_3$ and precipitated more or less completely (§ 134, 6*a*):

$$2MnCl_2 + 2NH_4OH = Mn(OH)_2 + (NH_4)_2MnCl_4$$
$$Mn(OH)_2 + 4NH_4Cl = (NH_4)_2MnCl_4 + 2NH_4OH$$
$$2(NH_4)_2MnCl_4 + 4NH_4OH + O + H_2O = 2Mn(OH)_3 + 8NH_4Cl$$
$$2MgCl_2 + 2NH_4OH = Mg(OH)_2 + NH_4MgCl_3 + HN_4Cl$$
$$Mg(OH)_2 + 3NH_4Cl = NH_4MgCl_3 + 2NH_4OH$$

Barium, calcium, and strontium are also precipitated as carbonate because the alkaline solution absorbs carbon dioxide from the air. As much as 15 mg. of barium may be present in this precipitate. (Curtman and Frankel, *J. Am. Soc.*, **33**, 724, 1911.) For detection of the barium see § 186, 8.

(*6*) Ammonium chloride lessens the solubility of $Al(OH)_3$ in the NH_4OH solution and effects an almost quantitative precipitation of that metal (§117).

(7) **NH_4OH** precipitates solutions of **Co**, **Ni** and **Zn**, but these precipitates are readily soluble in an excess of the **NH_4OH** (§116). To insure the presence of an excess of **NH_4OH** the odor should be noted after shaking the test tube and after the solution has been heated.

(8) The precipitates of the hydroxides of **Al**, **Cr** and **Fe‴** filter much more rapidly if the precipitation takes place from a hot solution (§124, 4 and 6*a*).

(9) In the presence of chromium the filtrate from the third group is usually of a slight violet color, due to the solution of a trace of chromium hydroxide in the **NH_4OH** (§125, 6*a*). Boiling the solution to remove excess of ammonia prevents this.

(10) A small portion of the filtrate of the second group after the removal of the **H_2S** by boiling should be tested for the presence of phosphates by ammonium molybdate (§75, 6*d*). If phosphates are found to be present, the method of analysis of the succeeding groups must be considerably modified. These modifications are fully discussed under §145 to §153.

§130. **Manipulation.**—The well washed precipitates of **Al**, **Cr**, **Fe‴** and **Mn‴** hydroxides are transferred to a small casserole or evaporating dish by piercing the point of the filter and washing the precipitate from the filter with as small an amount of water as possible.

Add **NaOH** and **H_2O_2** and boil for a minute or two or add **Na_2O_2** in small portions and boil until the chromium is completely oxidized as indicated by the yellow color.

$$2Cr(OH)_3 + 3Na_2O_2 = 2Na_2CrO_4 + 2H_2O + 2NaOH$$
$$Al(OH)_3 + NaOH = NaAlO_2 + 2H_2O$$

The alkaline solution is filtered (the filtrate is reserved to be tested for aluminum) and the remaining precipitate dissolved in dilute **HCl** or **H_2SO_4** with the addition of a few drops of **H_2O_2** if necessary to dissolve the manganese hydroxide.

$$Fe_2O_3 + 3H_2SO_4 = Fe_2(SO_4)_3 + 3H_2O$$
$$2Mn(OH)_3 + 2H_2SO_4 + H_2O_2 = 2MnSO_4 + 6H_2O + O_2$$

The iron is tested for by adding a few drops of ammonium or potassium sulphocyanate:

$$Fe_2(SO_4)_3 + 6KCNS = 2Fe(CNS)_3 + 3K_2SO_4$$

If iron has been found to be present, the original solution acidulated with **HCl** (or a few drops of the filtrate from the first group) should be tested with **KCNS** for the presence of ferric iron (§126, 6*b*) and with **$K_3Fe(CN)_6$** for the dark blue precipitate of **$Fe_3[Fe(CN)_6]_2$** indicating the presence of ferrous iron (§126, 6*b*):

$$3FeSO_4 + 2K_3Fe(CN)_6 = Fe_3[Fe(CN)_6]_2 + 3K_2SO_4$$

Manganese is tested for by boiling a portion of the solution with nitric

acid and PbO_2 or Pb_3O_4.* If manganese is present a solution of the reddish purple permanganic acid is obtained.

$$2MnSO_4 + 5PbO_2 + 6HNO_3 = 2HMnO_4 + 2PbSO_4 + 3Pb(NO_3)_2 + 2H_2O$$

The alkaline filtrate obtained after boiling the precipitated hydroxides with NaOH and H_2O_2 is acidified with acetic acid and one portion tested for chromium with $Pb(C_2H_3O_2)_2$ a yellow precipitate indicating chromium.

$$Na_2CrO_4 + Pb(C_2H_3O_2)_2 = PbCrO_4 + 2NaC_2H_3O_2 \text{ (§57, 6h)}$$

Another portion is tested for aluminum by adding $(NH_4)_2CO_3$ in excess and warming:

$$NaAlO_2 + 4HC_2H_3O_2 = Al(C_2H_3O_2)_3 + NaC_2H_3O_2$$
$$2Al(C_2H_3O_2)_3 + 3(NH_4)_2CO_3 + 3H_2O = 2Al(OH)_3 + 6NH_4(C_2H_3O_2) + 3CO_2$$

a white gelatinous precipitate being evidence of the presence of aluminum. A similar precipitate may also be obtained by adding excess of NH_4Cl to the alkaline solution:

$$2KAlO_2 + 2NH_4Cl + H_2O = Al_2O(OH)_4 + 2KCl + 2NH_3 \text{ (§124,6a)}$$

§ 131. *Notes.*—(*1*) Chromium hydroxide is oxidized by an alkaline oxidizing agent to a chromate. Sodium peroxide may be used or hydrogen peroxide and caustic soda which unite to form sodium peroxide. The same result may be obtained by fusing chromium hydroxide on a platinum foil with a mixture of equal parts of KNO_3 and Na_2CO_3.

$$2Cr(OH)_3 + 3KNO_3 + 2Na_2CO_3 = 2Na_2CrO_4 + 3KNO_2 + 2CO_2 + 3H_2O.$$

Aluminum is converted into sodium aluminate

$$2Al(OH)_3 + Na_2CO_3 = 2NaAlO_2 + 3H_2O + CO_2.$$

(*2*) Unless the precipitate of the hydroxides is a very dark green, due to the presence of a large amount of chromium, a portion of the precipitate should be dissolved in HCl and tested with KCNS for the presence of iron. The presence of a moderate amount of chromium does not interfere.

(*3*) In the absence of chromium the presence of more than traces of iron gives a brown color to the ammonium hydroxide precipitate (§126, 6*a*), aluminum hydroxide being a white gelatinous precipitate.

(*4*) Manganese remains undissolved when the mixed hydroxides are treated with sodium peroxide. When they are fused with KNO_3 and Na_2CO_3 the manganese is converted into the green manganate. (§ 134, 7). This dark green color is an excellent test for manganese which is almost invariably present with the hydroxides if it is in the solution of the unknown (§ 134, 6*a*). On treating the fused mass with water a green solution is obtained which turns purple on standing or cautiously acidifying with acetic acid.

(*a*) $K_2MnO_4 + 8HCl = MnCl_2 + 2KCl + 2Cl_2 + 4H_2O$

(*b*) $2K_2CrO_4 + 10HCl + 3C_2H_6O = 2CrCl_3 + 4KCl + 3C_2H_4O + 8H_2O$

(*5*) The presence of chromium as chromic salts is usually indicated by the green or bluish-green color of the original solution. Chromium as chromates (red or yellow) should be reduced to chromic salts by boiling with HCl and

* As PbO_2 and Pb_3O_4 frequently contain traces of manganese, the samples used when testing for manganese must first be tested as follows: Boil the oxide with dilute nitric acid and allow to settle. If the liquid is red, manganese is present. A pure sample of oxide must be obtained or the manganese removed by repeated boiling with nitric acid.

C_2H_6O before proceeding with the regular group separations (§ **125**, 6*e* and *f*). H_2S will effect this reduction but gives also a precipitate of sulphur which should be avoided when convenient to do so: $2K_2Cr_2O_7 + 16HCl + 6H_2S = 4CrCl_3 + 4KCl + 3S_2 + 14H_2O$.

(*6*) Too much stress cannot be laid upon the necessity for removing all the metals of one group before testing the filtrate for the metals of the next succeeding group. If through lack of sufficient H_2S or too much **HCl**, lead or antimony are not completely removed in the second group, they will give all the reactions for aluminum (§**57**, 6*a*, and §**70**, 6*a*); hence as a safeguard it is advised to test the white precipitate, indicating aluminum, with H_2S. A black or orange precipitate is evidence of unsatisfactory work and the student should repeat his analysis.

(*7*) The presence of a *trace* of white precipitate in the final test for aluminum may be due to the presence of that metal in the fixed alkali (§**124**, 6*a*, footnote), or it may be caused by the use of too concentrated fixed alkali, which may dissolve silica from the glass of the test tubes or remove it from the filter aper (§**249**, 5). The caustic soda solution may be tested by acidifying 10 c.c. with **HCl**, adding excess of $(NH_4)_2CO_3$ and warming. Note the amount of reci i-tate formed and do not re, ort aluminium unless a heavier precipitate is obtained in the analysis.

The Zinc Group (Fourth Group).

Cobalt, Nickel, Manganese, and Zinc.

§132. Cobalt. Co = 58.97. Usual valence two and three.

1. **Properties.**—*Specific gravity*, powder from the oxide reduced by hydrogen, mean of five samples, 8.957 (Rammelsberg, *Pogg.*, 1849, **78**, 93); *melting point*, 1480° (*Cir. B. S.*, **35**, 1915). Cobalt is similar to iron in appearance, is harder than **Fe** or **Ni**. It is malleable, very ductile and most tenacious of any metal, the wire being about twice as strong as iron wire (Deville, *A. Ch.*, 1856, (3), 46, 202). The fine powder oxidizes in the air quite rapidly and may even take fire spontaneously; in a compact mass it is but little tarnished in moist air. At a white heat it burns rapidly to Co_3O_4. It is attracted by the magnet and can be made magnetic, retaining (unlike steel) its magnetism at a white heat.

2. **Occurrence**—Cobalt does not occur in a free state, except in meteoric iron. It is found in linnaeite (Co_3S_4); skutterudite ($CoAs_3$); smaltite ($CoAs_2$); cobaltite (**CoAsS**); wad, asbolite (impure hydrous oxides of **Mn**, **Fe**, **Cu** and **Co**); and in a number of other rare minerals.

3. **Preparation.**—(*1*) By electrolysis of the chloride. (*2*) By heating with potassium or sodium. (*3*) By heating any of the oxides, hydroxides or the chloride in hydrogen gas. (*4*) By fusion of the oxalate under powdered glass. (*5*) Also reduced by carbon in various ways.

4. **Oxides** and **Hydroxides.**—*Cobaltous oxide*, **CoO**, is made (*1*) by heating any of its oxides or hydroxides in hydrogen to (not above) 350°; (*2*) by ignition of $Co(OH)_2$ or $CoCO_3$, air being excluded; (*3*) by heating Co_3O_4 to redness in a stream of CO_2 (Russell, *J. C.*, 1863, **16**, 51); (*4*) by heating any of the higher oxides to a white heat (Moissan, *A. Ch.*, 1880, (5), **21**, 242). *Cobaltous hydroxide* is made from cobaltous salts by precipitation with fixed alkalis; oxidizes if exposed to the air (6*a*). The most stable oxide is the *cobaltoso-cobaltic* (Co_3O_4) *tricobalt tetroxide*; it is made by heating any of the oxides or hydroxides, the carbonate, oxalate or nitrate to a dull-red heat in the air or in oxygen gas. Several oxide-hydroxides are known, *e. g.*, $Co_3O_2(OH)_4$, $Co_3O(OH)_6$, $Co_3O_3(OH)_2$. *Cobaltic oxide*, Co_2O_3, is made by heating the nitrate just hot enough for decomposition, but not hot enough to form Co_3O_4. *Cobaltic hydroxide*, $Co(OH)_3$, is made by treating any cobaltous salt with **Cl**, **HClO**, **Br** or **I** in presence of a fixed alkali or alkali carbonate. It dissolves in **HCl** with evolution of chlorine, in H_2SO_4 with evolution of oxygen, forming a cobaltous salt. CoO_2 has not yet been isolated, but McConnell and Hanes (*J. C.*, 1897, **71**, 584) have shown that it exists as H_2CoO_3 and in certain cobaltites.

5. **Solubilities.**—*a.—Metal.*—Slowly soluble on warming in dilute **HCl** or H_2SO_4, more rapidly in HNO_3, not oxidized on exposure to the air or when heated in contact with alkalis. Like iron, it may exist in a passive form (Nickles, *J. pr.*, 1854, **61**, 168; St. Edme, *C. r.*, 1889, **109**, 304). With the halogens it forms cobaltous compounds (Hartley, *J. C.*, 1874, **27**, 501). *b.—Oxides* and *hydroxides.*—Cobaltous oxide (gray-green) and hydroxide (rose-red) are insoluble in water; soluble in acids, in ammonium hydroxide, and in concentrated solutions of the fixed alkalis when heated (Zimmerman, *A.*, 1886, **232**, 324); the various higher oxides and hydroxides are insoluble in ammonium hydroxide or chloride (separation from nickelous hydroxide after treating with iodine in alkaline mixture) (Donath, *Z.*, 1881, **20**, 386), and are decomposed by acids, evolving oxygen with non-reducing acids, or a halogen from the halogen acids, and forming cobaltous salts. Co_3O_4 is said to be soluble in acids with great difficulty (Gibbs and Geuth, *Am. S.*, 1857, (2), **23**, 257). *c.—Salts.*—Cobalt forms two classes of salts: *cobaltous*, derived from **CoO**, and *cobaltic*, from Co_2O_3. The latter salts are quite unstable, decomposing in most cases at ordinary temperatures, forming cobaltous salts. The cobaltous salts show a remarkable variation of color. The crystallized salts with their water of crystallization are pink; the anhydrous salts are lilac-blue. In dilute solution the salts are pink, but most of them are blue when concentrated or in presence of strong acid. A dilute solution of the chloride spreads colorless upon white paper, turning blue upon heating and colorless again upon cooling, used as "sympathetic ink."

Cobaltous nitrate and acetate are *deliquescent*; chloride, hygroscopic; sulphate, efflorescent. The chloride vaporizes, undecomposed, at a high temperature.

The carbonate, sulphide, phosphate, borate, oxalate, cyanide, ferrocyanide and ferricyanide are *insoluble* in water. The potassium-cobaltous oxide is insoluble; the ammonio-cobaltous oxide, and the double cyanides of cobalt and the alkali metals, soluble in water. Alcohol dissolves the chloride and nitrate; ether dissolves the chloride, sparingly, more so if the ether be saturated with **HCl** gas (separation from **Ni**) (Piñerúa, *C. r.*, 1897, **124**, 862). Most of the salts insoluble in water form soluble compounds with ammonium hydroxide.

6. **Reactions.** *a.*—The **fixed alkali hydroxides** precipitate, from solutions of cobaltous salts, blue *basic salts*, which absorb oxygen from the air and turn olive green, as cobaltoso-cobaltic hydroxide; or if boiled before oxidation in the air, become rose-red, as *cobaltous hydroxide*, $Co(OH)_2$. The cobaltous hydroxide is not soluble in excess of the reagent, but is somewhat soluble in a hot concentrated solution of **KOH** or **NaOH** (distinction from **Ni**) Reichel, *Z.*, 1880, **19**, 468). The cold solution is blue, the color being more intense when hot and especially if a little glycerine is present. On standing it turns green, then red, the changes being more rapid if a little hydrogen peroxide solution is added. Copper also gives a blue solution but does not give the other color changes. Donath, *Z.*, **40**, 137. Freshly precipitated $Pb(OH)_2$, $Zn(OH)_2$, and **HgO** precipitate $Co(OH)_2$ from solutions of cobaltous salts at 100°. Ammonium hydroxide causes the same precipitate as the fixed alkalis; incomplete, even at first, because of the ammonium salt formed in the reaction, and soluble in excess of the reagent to a solution which turns brown in the air by combination with oxygen, and is not precipitated by potassium hydroxide. The reaction of the precipitate with ammonium salts forms soluble double salts (as with magnesium); the reaction of the

precipitate with ammonium hydroxide produces, in different conditions, different soluble compounds noted for their bright colors, as $(NH_3)_4CoCl_2$, $(NH_3)_6CoCl_2$, $(NH_3)_4CoCl_3$, etc.

Alkali **carbonates** precipitate *cobaltous basic-carbonate*, $Co_8O_5(CO_3)_3$, peach-red, which when boiled loses carbonic anhydride and acquires a violet, or, if the reagent be in excess, a blue color. The precipitate is soluble in ammonium carbonate and very slightly soluble in fixed alkali carbonates. **Carbonates** of **Ba**, **Sr**, **Ca**, or **Mg** do not precipitate cobaltous chloride or nitrate in the cold (separation from **Fe‴**, **Al**, and **Cr‴**), but by prolonged boiling they precipitate them completely. However, if a solution of a cobaltous salt be treated with chlorine, a cobaltic salt is formed (*5a*), which is precipitated in the cold on digestion with $BaCO_3$ (distinction from **Ni**).

b.—**Oxalic acid** and **oxalates** precipitate reddish-white *cobaltous oxalate*, CoC_2O_4, soluble in mineral acids and in ammonium hydroxide.

Alkali **cyanides**—as **KCN**—precipitate the brownish-white *cobaltous cyanide*, $Co(CN)_2$, soluble in hydrochloric acid, not in acetic or in hydrocyanic acid, soluble in excess of the reagent, as double cyanides of cobalt and alkali metals—$(KCN)_2Co(CN)_2$—potassium cobaltous cyanide, the solution having a brown color: $CoCl_2 + 2KCN = Co(CN)_2 + 2KCl$. Then $Co(CN)_2 + 2KCN = (KCN)_2Co(CN)_2$. Dilute acids, *without digestion*, reprecipitate cobaltous cyanide from this solution (the same as with **Ni**): $(KCN)_2Co(CN)_2 + 2HCl = Co(CN)_2 + 2HCN + 2KCl$. But if the solution, with excess of the alkali cyanide and with a drop or two of hydrochloric acid,* insuring free **HCN**, be now *digested* hot for some time, the cobaltous cyanide is oxidized and converted into alkali *cobalticyanide*—as $K_3Co(CN)_6$—corresponding to ferricyanides, *but having no corresponding nickel* compound:

$$4Co(CN)_2 + 4HCN + O_2 = 4Co(CN)_3 \text{ (cobaltic cyanide)} + 2H_2O$$
$$Co(CN)_3 + 3KCN = K_3Co(CN)_6 \text{ (potassium cobalticyanide)}.$$

In the latter solution neither alkalies nor acids precipitate the cobalt (*important distinction from nickel,* whose solution remains $(KCN)_2Ni(CN)_2$, and which, after digestion as above is precipitated). The potassium cobalticyanide solution, after removal of the **Ni**, may be precipitated with $HgNO_3$ (Gibbs, *J. C.*, 1874, **27**, 92). The oxidation of the cobalt may be hastened by the presence of chromic acid, which is

* Moore (*C. N.*, 1887, **56**, 3) adds glacial phosphoric acid to the neutral solutions of cobalt and nickel, until the precipitate first formed begins to redissolve; then he adds **KCN** and boils, continuing the boiling and addition of **KCN** until **KOH** fails to give a precipitate. He then warms with excess of bromine in presence of **KOH**, whereupon the nickel is completely precipitated leaving the cobalt in solution. See also Hambly (*C. N.*, 1892, **65**, 289).

reduced to trivalent chromium compound: $6Co(CN)_2 + 24KCN + 2CrO_3 + 3H_2O = 6K_3Co(CN)_6 + Cr_2O_3 + 6KOH$ (McCulloch, *C. N.*, 1889, **59**, 51), also by means of **NaClO** or **NaBrO** produced by passing chlorine into caustic soda or adding bromide to the alkali.

Ferrocyanides, as $K_4Fe(CN)_6$, precipitate *cobaltous ferrocyanide*, $Co_2Fe(CN)_6$, gray-green, insoluble in acids. Ferricyanides, as $K_3Fe(CN)_6$, precipitate *cobaltous ferricyanide*, $Co_3(Fe(CN)_6)_2$, brownish-red, insoluble in acids. But a more distinctive test is made by adding *ammonium chloride* and *hydroxide*, with the ferricyanide, when a *blood-red color* is obtained, in evidence of cobalt (distinction from nickel). **Potassium xanthate** forms a green precipitate in neutral or slightly acid solutions of cobalt salts (§133, 6b).

Nitroso-β-naphthol completely precipitates solutions of **Cu**, **Fe**, and **Co**; **Ag**, **Sn**, and **Bi** salts are partially precipitated; and **Pb**, **Hg**, **As**, **Sb**, **Cd**, **Al**, **Cr**, **Mn**, **Ni**, **Zn**, **Ca**, **Mg**, and **Gl** remain in solution (Burgass, *Z. angew.*, 1896, 596). In analysis for the separation of *cobalt* and *nickel* it is recommended to proceed as follows: The solution of the metals preferably as sulphates or chlorides is acidulated with hydrochloric acid and treated with a hot solution of nitroso-β-naphthol in 50 per cent acetic acid, until the whole of the *cobalt* is precipitated. The brick-red precipitate is then washed with cold **HCl**, then with hot 12 per cent **HCl**, and finally with water. The separation is *quantitative*. The precipitate may be ignited in air to the oxide or with oxalic acid in an atmosphere of hydrogen and weighed as the metal. For qualitative purposes the cobalt in the precipitate may be identified by the color of the borax bead (7). The nickel in the filtrate may be precipitated by hydrosulphuric acid and identified by the usual tests (Knorre, *B.*, 1887, **20**, 283 and *Z. angew.*, 1893, 264).

Ammonium Thiocyanate in concentrated solutions of cobalt produces a brilliant blue color which disappears on dilution with water. On the addition of amyl alcohol and ether in equal portions and shaking, the layer of alcohol and ether becomes blue. The test is very delicate especially if the cobalt solution is concentrated. Nickel salts produce no coloration of the amyl alcohol and ether, but iron interferes because the red $Fe(CNS)_3$ is dissolved by the alcohol. By the addition of 2 or 3 c.c. of concentrated ammonium acetate solution and 2 or 3 drops of 50 per cent tartaric acid solution, the red color of the $Fe(CNS)_3$ may be removed. The blue color is probably due to the undissociated salt $(NH_4)_2[Co(CNS)_4]$ which is soluble in ether and amyl alcohol (Vogel *Ber.* **12**, 2314. Treadwell, *Z. An. Ch.* **26** (1901), 105).

Ammonium thiocyanate may be employed for the separation of nickel and cobalt (Rosenheim and Cohen, *B.*, **33**, 111, and Rosenheim and Huldshinsky, *B.*, **34**, 2050), 12 grams of NH_4CNS are added to the nitric acid solution of the metals the volume being 15-20 c.c. Cobalt produces a deep

blue compound of the formula $R_2Co(CNS)_4$ in which **R** is an alkali metal. This blue compound may be extracted by a mixture of 25 vol. ether and 1 vol. amyl alcohol.

c.—**Potassium nitrite** forms with both *cobaltous* and *nickelous* salts the double nitrites, $Co(NO_2)_2.2KNO_2$ and $Ni(NO_2)_2.2KNO_2$, soluble. The nickel compound is very stable, but if the cobalt compound, strongly acidulated with acetic acid, be warmed and allowed to stand for some time, preferably twenty-four hours; the cobalt is completely precipitated as the yellow crystalline potassium cobaltic nitrite, $Co(NO_2)_3.3KNO_2$ (separation from **Ni**): $CoCl_2 + 6KNO_2 + HC_2H_3O_2 + HNO_2 = Co(NO_2)_3.3KNO_2 + 2KCl + KC_2H_3O_2 + H_2O + NO$.

d.—**Phosphates,** as Na_2HPO_4, precipitate cobaltous salts as the reddish *cobaltous phosphate*, $CoHPO_4$, soluble in acids and in ammonium hydroxide. Sodium **pyrophosphate** forms a gelatinous precipitate with solutions of cobalt salts, soluble in excess of the reagent. The addition of acetic acid causes a precipitation of the cobalt even in the presence of tartrates (separation from **Ni**, but not from **Mn** or **Fe**) (Vortmann, *B.*, 1888, **21**, 1103). If a solution of cobaltous salt be treated with a saturated solution of **ammonium phosphate** and hydrochloric acid, and when hot treated with an excess of ammonium hydroxide, a bluish precipitate of $CoNH_4PO_4$ will appear on stirring (separation from nickel*) (Clark, *C. N.*, 1883, **48**, 262; Hope, *J. Soc. Ind.*, 1890, **9**, 375).

e.—**Hydrosulphuric acid,** with normal cobaltous salts, gradually and imperfectly precipitates the black *cobalt sulphide*, **CoS** ; from cobalt acetate, the precipitation is more prompt, and is complete; but in presence of mineral acids, as in the second group precipitation, no precipitate is made. Immediate precipitation takes place with hydrosulphuric acid acting upon solutions of cobaltous salts in ammonium hydroxide. When formed, the precipitate is scarcely at all soluble in dilute hydrochloric acid or in acetic acid; slowly soluble in moderately concentrated hydrochloric acid; readily soluble in nitric acid; and most easily in nitrohydrochloric acid. By exposure to the air, the recent cobaltous sulphide is gradually oxidized to cobalt sulphate, soluble, as occurs with iron sulphide (§**126**, 6*e*). **Alkali sulphides** precipitate immediately and perfectly the black cobaltous sulphide, described above, insoluble in excess of the reagent. When cobaltous salts are boiled with **sodium thiosulphate** a portion of the cobalt is precipitated as the black sulphide.

f.—The higher oxides of cobalt and cobaltic salts are reduced by warming with halogen acids, liberating the corresponding halogens (**HCl** does not reduce the cobalt in $K_3Co(CN)_6$).

g.—Soluble **arsenites** and **arsenates** precipitate cobaltous salts, forming the corresponding *cobalt arsenites* or *arsenates*, bluish-white, soluble in ammonium hydroxide or in acids, including arsenic acid. *h.*—Soluble **chromates** precipitate *cobaltous chromate*, yellowish-brown, soluble in ammonium hydroxide and

* Krauss (*Z.*, 1891, **30**, 227) gives a good review of the most important methods for the separation of cobalt and nickel.

in acids, including chromic acid. No precipitate is formed with potassium dichromate. *i*.—$KMnO_4$ added to an ammoniacal solution of cobaltous salts oxidizes the cobalt and prevents its precipitation by **KOH** (separation from **Ni**) (Delvaux, *C. r.*, 1881, **92**, 723).

j.—Cobaltous salts in ammoniacal solution, warmed with H_2O_2 and then rendered acid with acetic acid, are precipitated by ammonium molybdate (separation from **Ni**) (Carnot, *C. r.*, 1889, **109**, 109).

7. **Ignition.**—**In the bead** of borax, and in that of microcosmic salt, with oxidizing and with reducing flames, cobalt gives an intense *blue* color. The blue bead of copper changes to brown in the reducing flame. If strongly saturated, the bead may appear black from intensity of color, but will give a blue powder. This important test is most delicate with the borax bead. Manganese, copper, nickel, or iron interfere somewhat. By **ignition,** with sodium carbonate on charcoal or with the reducing flame, compounds of cobalt are reduced to the metal (magnetic). Cobaltous oxide dissolves in melted glass and in other vitreous substances, coloring the mass blue—used to cut off the light of yellow flames (§**205**, 7). The black cobaltoso-cobaltic oxide, Co_3O_4, as left by ignition of cobaltous oxide or nitrate, combines or mixes, by ignition, with zinc oxide from zinc compounds to form a green mass, with aluminum compounds a blue, and with magnesium compounds a pink mass.

8. **Detection.**—After removal of the metals of the first three groups cobalt is precipitated by H_2S in ammoniacal solution with **Ni**, **Mn** and **Zn**. The sulphides are digested with cold dilute **HCl** which dissolves the **Mn** and **Zn**. The borax bead test (7) is now made upon the remaining black precipitate, and if **Ni** be not present in great excess * the characteristic blue bead is obtained. If the nickel be present in such quantities as to obscure the blue borax bead the sulphides are dissolved in hot conc. **HCl**, using a few drops of HNO_3. The solution is heated to decompose all the nitric acid and, after dilution, the cobalt is precipitated with nitroso-β-naphthol, according to directions given in 6*b*, and further identified by the bead test.

The NH_4CNS test (§132, 6*b*) and the $NaHCO_3$ and H_2O_2 test (§140) may also be obtained.

9. **Estimation.**—(*1*) As metallic cobalt, all compounds that may be reduced by ignition in hydrogen gas, *e. g.* $CoCl_2$, $Co(NO_3)_2$, $CoCO_3$, and all oxides and hydroxides. (*2*) As **CoO**, all soluble cobalt salts, all salts whose acids are expelled or destroyed by ignition, all oxides and hydroxides. The salt is converted into $Co(OH)_2$ by precipitation with a fixed alkali, and ignited in a stream of CO_2. The carbonate and nitrate may be ignited directly in CO_2, and organic salts are first ignited in the air until the carbon is oxidized, and then again ignited in CO_2. (*3*) After converting into a sulphate it is ignited at a dull-red heat and weighed as a sulphate. (*4*) After converting into the oxalate, titrated with $KMnO_4$. (*5*) In presence of nickel, it is oxidized in alkaline solution by H_2O_2, **KI** and **HCl** are added, and the liberated iodine titrated with sodium thiosulphate (Fischer, *C. C.*, 1889, 116). (*6*) Electrolytically. (*7*) Separated

* If more than ten parts of nickel are present to one part of cobalt, the characteristic blue bead is not obtained.

from nickel by **nitroso-β-naphthol,** and after ignition in hydrogen weighed as the metal (6b).

10. **Oxidation.**—Co″ is oxidized to Co‴ in presence of a fixed alkali by PbO_2, Cl, KClO, Br, KBrO, I and H_2O_2*; in presence of acetic acid by KNO_2 (6c). Co‴ is reduced to Co″ by $H_2C_2O_4$, H_3PO_2, H_2S, H_2SO_3, HCl, HBr, and HI. Metallic cobalt is precipitated from solution of $CoCl_2$ by Zn, Cd, and Mg.

§133. Nickel. Ni = 58.70. Usual valence two and three.

1. **Properties.**—*Specific gravity*, 8.9 (Schroeder, *Pogg.*, 1859, **106**, 226). *Melting point*, 1452° (*Cir. B. S.*, **35**, 1915). It is a hard white metal, capable of taking a high polish; malleable, ductile and very tenacious, forming wire stronger than iron but not quite so strong as cobalt (§ **132**, 1). It does not oxidize in dry or moist air at ordinary temperatures. It is magnetic but loses its magnetism like steel on heating to redness (Gangain, *C. r.*, 1876, **83**, 661). It burns with incandescence when heated in O, Cl, Br, or S. It is much used in plating other metals, in making coins of small denominations, in hardening armor plate, projectiles, etc. The presence of small amounts of phosphorus or arsenic renders it much more fusible, without destroying its ductility; a larger amount makes it brittle.

2. **Occurrence.**—Nickel almost always occurs in nature together with cobalt. It is found as millerite, (NiS); pentlandite (FeNi)S; niccolite (NiAs); garnierite (variable, perhaps $H_2(NiMg)SiO_4 + xH_2O$); frequently in pyrrhotite, (Fe_nS_{n+1} with Ni) and in numerous other rarer minerals.

3. **Preparation.**—(*1*) By electrolysis. (*2*) By heating in a stream of hydrogen. The oxide is reduced in this manner at 270° (W. Müller, *Pogg.*, 1869, **136**, 51). (*3*) By fusing the oxalate under powdered glass (CO_2 being given off). (*4*) Reduction by igniting in CO. (*5*) Reduction by fusing with carbon in a variety of methods. (*6*) By heating the carbonyl,† $Ni(CO)_4$ to 200°.

4. **Oxides** and **Hydroxides.**—*Nickelous oxide* is formed when the carbonate, nitrate, or any of its oxides or hydroxides are strongly ignited. *Nickelous hydroxide* is formed by precipitation of nickelous salts with fixed alkalis. *Nickelic oxide*, Ni_2O_3, is made from $NiCO_3$, $Ni(NO_3)_2$ or NiO by heating in the air not quite to redness, with constant stirring. It is changed to NiO at a red heat. Nickelic hydroxide, $Ni(OH)_3$, is formed by treating nickelous salts first with a fixed alkali hydroxide or carbonate and then with Cl, NaClO, Br or NaBrO (not formed by iodine), a black powder forming no corresponding salts (Campbell and Trowbridge, *J. Anal.*, 1893, **7**, 301). A trinickelic tetroxide, Ni_3O_4, magnetic (corresponding to Co_3O_4, Fe_3O_4, Mn_3O_4 and Pb_3O_4), is formed, according to Baubigny (*C. r.*, 1878, **87**, 1082), by heating $NiCl_2$ in oxygen gas at from 350° to 440°; and by heating Ni_2O_3 in hydrogen at 190° (Moissan, *A. Ch.*, 1880, (5), **21**, 199).

5. **Solubilities.**—*a.—Metal.*—Hydrochloric or sulphuric acid, dilute or concentrated, attacks nickel but slowly (Tissier, *C. r.*, 1860, **50**, 106); dilute nitric acid dissolves it readily, while towards concentrated nitric acid it acts very similar to passive iron (Deville, *C. r.*, 1854, **38**, 284). It is not attacked when heated in contact with the alkali hydroxides or carbonates. *b.—Oxides* and

* Durant, *C. N.*, 1897, **75**, 43.

† Nickel carbonyl is prepared by heating the nickel ore in a current of CO. It is a liquid, sp. gr. 1.3185, boiling at 43° and freezing at −25°. When heated to 200° it is decomposed into Ni and CO (Berthelot, *C. r.*, 1891, **112**, 1343; **113**, 679; Mond, *J. Soc. Ind.*, 1892, **11**, 750).

hydroxides.—Nickelous oxide and hydroxide are insoluble in water or fixed alkalis, soluble in ammonium hydroxide and in acids. Nickelic oxides and hydroxides are dissolved by acids with reduction to nickelous salts, with halogen acids the corresponding halogens are liberated. The moist nickelic hydroxide, formed by the action of **Cl**, **Br**, etc., in alkaline solution, after washing with hot water liberates free iodine from potassium iodide (distinction from cobalt). Nickelic hydroxide when treated with dilute sulphuric acid forms $NiSO_4$, oxygen being evolved. With nitric acid the action is similar, distinction from cobaltic hydroxide, which requires a more concentrated acid to effect a similar reduction. *c. Salts.*—The salts of nickel have a delicate green **color** in crystals and in solution; when anhydrous, they are yellow. The nitrate and chloride are **deliquescent** or **efflorescent**, according to the hygrometric state of the atmosphere; the acetate is efflorescent. The chloride **vaporizes** at high temperatures.

The carbonate, sulphide, phosphate, borate, oxalate, cyanide, ferrocyanide and ferricyanide are **insoluble**; the double cyanides of nickel and alkali metals, soluble in water. The chloride is soluble in alcohol, and the nitrate in dilute alcohol. Most salts of nickel form soluble compounds by action of ammonium hydroxide.

6. **Reactions.** *a.*—**Alkali hydroxides** precipitate solutions of nickel salts as *nickel hydroxide*, $Ni(OH)_2$, pale green, not oxidized by exposure to the air (§132, 6*a*), insoluble in excess of the fixed alkalis (distinction from zinc), soluble in ammonium hydroxide or ammonium salts, forming a greenish-blue to violet-blue solution. Excess of fixed alkali hydroxide will slowly precipitate nickel hydroxide from the ammoniacal solutions (distinction from cobalt). **Alkali carbonates** precipitate green *basic nickelous carbonate*, $Ni_3(OH)_6(CO_3)_2$ (composition not constant), soluble in ammonium hydroxide or ammonium salts, with blue or greenish-blue color. Carbonates of **Ba**, **Sr**, **Ca**, and **Mg** are without action on nickelous chloride or nitrate in the cold (distinction from Fe''', **Al**, and Cr'''), but on boiling precipitate the whole of the nickel.

b.—**Oxalic acid** and **oxalates** precipitate, very slowly but almost completely, after twenty-four hours, nickel oxalate, green. Alkali **cyanides**, as **KCN**, precipitate *nickel cyanide*, $Ni(CN)_2$, yellowish-green, insoluble in hydrocyanic acid, and in cold dilute hydrochloric acid; dissolving in excess of the cyanide, by formation of soluble double cyanides, as potassium nickel cyanide $(KCN)_2Ni(CN)_2$. The equation of the change corresponds exactly to that for *cobalt* (§132, 6*b*); and the solution of double cyanide is reprecipitated as $Ni(CN)_2$ by a careful addition of **acids** (like cobalt); but hot digestion, with the liberated hydrocyanic acid, forms no compound corresponding to cobalticyanides, and does not prevent precipitation by acids (distinction from cobalt). It will be observed that excess of hydrochloric or sulphuric acid will dissolve the precipitate of $Ni(CN)_2$. If an oxidizing agent such as **NaClO** or **NaBrO** be added to the alkaline solution of the double cyanide, the nickel will be oxidized and precipitated (separation from cobalt), as $Ni_2O_3.3H_2O$, according to the following equation:

$$K_2Ni(CN)_4 + NaBrO + NaOH = Ni_2O_3 \cdot 3H_2O$$

Ferrocyanides, as $K_4Fe(CN)_6$, precipitate a greenish-white *nickel ferrocyanide*, $Ni_2Fe(CN)_6$, insoluble in acids, soluble in ammonium hydroxide, decomposed by fixed alkalis. **Ferricyanides** precipitate greenish-yellow *nickel ferricyanide*, insoluble in acids, soluble in ammonium hydroxide to a green solution (§132, 6b).

A solution of **nitroferricyanide** precipitates solutions of cobalt and nickel salts, the latter being soluble in dilute ammonium hydroxide (Cavalli, *Gazzetta*, 1897, **27**, ii, 95).

A solution of **potassium xanthate** precipitates neutral solutions of nickel and cobalt, the former being soluble in ammonium hydroxide (distinction), from which solution it is precipitated by $(NH_4)_2S$ (Phipson, *C. N.*, 1877, **36**, 150). The xanthate also precipitates nickel in alkaline solution in presence of $Na_4P_2O_7$ (a separation from Fe‴) (Campbell and Andrews, *J. Am. Soc.*, 1895, **17**, 125).

Nickel salts are *not* precipitated by an acetic acid solution of **nitroso-β-naphthol** (separation from cobalt) (Knorre, *B.*, 1885, **18**, 702).

c.—**Potassium nitrite** in presence of acetic acid does not oxidize nickelous compounds (distinction from cobalt). *d.*—**Sodium phosphate,** Na_2HPO_4, precipitates *nickel phosphate*, $Ni_3(PO_4)_2$, greenish-white.

e.—**Hydrosulphuric acid** precipitates from neutral solutions of nickel salts a portion of the nickel as *nickel sulphide*, black (Baubigny, *C. r.*, 1882, **94**, 1183; **95**, 34). The precipitation takes place slowly, and from nickelous acetate is complete. In the presence of mineral acids no precipitation takes place. **Alkali sulphides** precipitate the whole of the nickel, as the black sulphide. Although precipitation is prevented by free acids, the precipitate, once formed, is nearly insoluble in acetic or in dilute hydrochloric acids; slowly dissolved by concentrated hydrochloric acid, readily by nitric or nitro-hydrochloric.

Nickel sulphide, **NiS**, is partially soluble in yellow ammonium sulphide,* **from** which brown-colored solution it is precipitated (*gray*, black mixed with sulphur) on addition of acetic acid (distinction from cobalt). It is insoluble in the monosulphide and is completely precipitated by passing hydrogen sulphide through an ammoniacal solution in the absence of air or oxidizing agents (Noyes, Bray and Spear, *J. Am. Soc.*, **30**, 497). Freshly precipitated nickel sulphide is soluble in **KCN** and reprecipitated as $Ni(CN)_2$ on adding **HCl** or H_2SO_4 (separation from cobalt) (Guyard, *Bl.*, 1876, (2), **25**, 509). When nickel salts are boiled with a solution of $Na_2S_2O_3$, a portion of the nickel is precipitated as the black sulphide.

f.—The halogen acids reduce the higher oxides of nickel to nickelous salts with liberation of the corresponding halogen. Potassium iodide added to freshly precipitated nickelic hydroxide gives free iodine (distinction from cobalt).

g.—Nickel salts are precipitated by **arsenites** and **arsenates,** white or greenish-white, soluble in acids, including arsenic acid. *h.*—Potassium **chromate** precipitates basic nickel chromate, yellow, soluble in acids, including chromic acid (Schmidt, *A.*, 1870, **156**, 19). $K_2Cr_2O_7$ forms no precipitate.

7. **Ignition.**—Nickel compounds dissolve clear in the **borax bead,** giving with the oxidizing flame a purple-red or violet color while hot, becoming yellowish-brown when cold; with the reducing flame, fading to a turbid gray, from reduced metallic nickel, and finally becoming colorless. The addition of any potassium salt, as potassium nitrate, causes the borax bead to take a dark purple or blue color, clearest in the oxidizing flame. With **microcosmic salt,**

*Hare (*J. Am. Soc.*, 1895, **17**, 537) adds tartaric acid to the solutions of nickel and cobalt, and an excess of sodium hydroxide. He then passes in H_2S. The cobalt is completely precipitated while the nickel remains in solution, and can be precipitated upon acidulating the filtrate.

nickel gives a reddish-brown bead, cooling to a pale reddish-yellow, the colors being alike in both flames. Hence, with this reagent, in the reducing flame, the color of nickel may be recognized in presence of *iron* and *manganese*, which are colorless in the reducing flame; but *cobalt* effectually obscures the bead test for nickel. The yellow-red of *copper* in the reducing flame, persisting in beads of microcosmic salt, also masks the bead test for nickel. By ignition with sodium carbonate on charcoal, compounds of nickel are reduced to the metal, slightly attracted by the *magnet*.

8. **Detection.**—We proceed exactly as with cobalt for the **nitroso-β naphthol** precipitation. The **Ni** remains in the filtrate and can be precipitated with H_2S (after neutralizing with NH_4OH), and its presence confirmed by the usual tests. Or dissolve the sulphides of **Ni** and **Co** in HNO_3, evaporate nearly to dryness, add an excess of **KOH** or Na_2CO_3, boil, add bromine water and boil to complete oxidation of the **Co** and **Ni**, filter, wash *thoroughly* with hot water and add hot solution of **KI** to the precipitate on the filter paper. Free iodine (test with CS_2) is evidence of the presence of nickel.

Nickel may also be detected in the presence of cobalt as follows:—Dissolve the sulphides of **Ni** and **Co** in aqua regia, boil out the excess of chlorine, neutralizing with **KOH** and add **KCN** in slight excess. Add **NaClO** or **NaBrO** and warm. The nickel is precipitated as the brown hydrated oxide $Ni_2O_3.3H_2O$.

Dimethylglyoxime produces a red crystalline precipitate which forms the most sensitive test known for detecting nickel in the presence of cobalt. The reagent is prepared by dissolving 1 gram of the dimethyglyoxime in 100 c.c. of 98% alcohol. The solution should be made slightly alkaline with ammonia and boiled after adding a few drops of the reagent. The following reactions take place:

$$2(CH_3)_2C_2N_2O_2H_2 + NiCl_2 + 2NH_4OH = 2NH_4Cl + [(CH_3)_2C_2N_2O_2H]_2Ni + 2H_2O$$

If the amount of nickel is small the solution at first becomes yellow and on cooling deposits red needles. The test is sensitive to nickel when present in 400,000 parts of water (L. Tschugaeff *Ber.* **38** (1905), 2520). Ten times as much cobalt may be present but in the presence of larger quantities of cobalt the following procedure is followed. Excess of ammonia is added to the cobalt solution and then a few cubic centimeters of hydrogen peroxide. The solution is boiled to decompose the excess of hydrogen peroxide. Dimethylglyoxime is added and the solution again boiled. If a small amount of nickel is present a red scum is formed on the solution and red crystals form on the sides of the beaker. On filtering the solution the red precipitate is readily observed on the filter paper.

9. **Estimation.***—(*1*) Nickel hydroxide, oxide, carbonate or nitrate is ignited at a white heat and weighed as **NiO**. (*2*) It is converted into the sulphate and

* Goulal (*Z. angew.*, 1898, 177) gives a summary of the methods proposed for the volumetric estimation of nickel.

deposited on platinum as the free metal by the electric current. (*3*) Volumetrically. By titration in a slightly alkaline solution with **KCN**, using a small amount of freshly precipitated **AgI** as an indicator (Campbell and Andrews, *J. Am. Soc.*, 1895, **17**, 127).

10. **Oxidation.**—**Ni″** is changed to **Ni‴** in presence of fixed alkalis by **Cl**, **NaClO**, **Br**, and **NaBrO** (not by **I**, distinction from cobalt, Donath, *B.*, 1879, **12**, 1868). **Ni‴** is reduced to **Ni″** by all non-reducing acids with evolution of oxygen; by reducing acids, $H_2C_2O_4$ is oxidized to CO_2, HNO_2 to HNO_3, H_3PO_2 to H_3PO_4, H_2S to **S**, H_2SO_3 to H_2SO_4, **HCl** to **Cl**, **HBr** to **Br**, **HI** to **I**, **HCNS** to **HCN** and H_2SO_4, $H_4Fe(CN)_6$ to $H_3Fe(CN)_6$. **Ni″** is reduced to the metal by finely divided **Zn**, **Cd**, and **Sn**.

§134. Manganese. Mn = 54.93. Valence two, three, four, six and seven.

1. **Properties.**—*Specific gravity*, 7.392 (Glatzel, *Ber.*, 1889). *Melting point*, 1260° (*Cir. B. S.*, **35**, 1915). *Boiling point*, 1900° (v. d. Weyde, *Ber.* **44**, 1879). It is a brittle metal, having the general appearance of cast iron, non-magnetic, takes a high polish. According to Deville it has a reddish appearance. It is readily oxidized, decomposing water at but little above the ordinary temperature (Deville, *A. Ch.*, 1856, (3), **46**, 199). It is used largely as ferromanganese in the manufacture of Bessemer steel.

Oxides and hydroxides of manganese exist as dyad, triad, and tetrad; the salts exist most commonly as the dyad with some unstable triad and tetrad salts; as an acid it is a hexad in manganates and a heptad in permanganates.

2. **Occurrence.**—Not found native. It accompanies nearly all iron ores. Its chief ore is pyrolusite (MnO_2). It is also found as braunite, ($3Mn_2O_3.MnSiO_3$); hausmannite, (Mn_3O_4); manganite, ($Mn_2O_3.H_2O$); rhodocrosite, $MnCO_3$; alabandite, (**MnS**); and as a constituent of many other minerals.

3. **Preparation.**—(*1*) By electrolysis of the chloride. (*2*) By reduction with metallic sodium or magnesium (Glatzel, *B.*, 1889, **22**, 2857). (*3*) By reduction with some form of carbon. It has not been reduced by hydrogen. (*4*) By ignition with aluminum (Goldschmidt, *A.*, 1898, **301**, 19).

4. **Oxides** and **Hydroxides.**—(*a*) **Manganous oxide, MnO**, represents the only base capable of forming stable manganese salts. It is formed (*1*) by simple ignition of $Mn(OH)_2$, $MnCO_3$ or MnC_2O_4, air being excluded; (*2*) by ignition of any of the higher oxides of manganese with hydrogen in a closed tube (Moissan, *A. Ch.*, 1880, (5), **21**, 199). If prepared at as low a temperature as practicable, it is a dark gray or greenish-gray powder, and oxidizes quickly in the air to Mn_3O_4. If prepared at a higher heat it is more stable. **Manganous hydroxide, Mn(OH)$_2$**, is formed from manganous salts by precipitation with alkalis. It quickly oxidizes in the air, forming **MnO(OH)**, thus changing from white to brown. (*b*) **Manganic oxide, Mn_2O_3**, is formed by heating any of the oxides or hydroxides to a red heat in oxygen gas or in air (Schnieder, *Pogg.*, 1859, **107**, 605). **Manganic oxide-hydroxide, MnO(OH)**, is formed (*1*) by oxidation of $Mn(OH)_2$ in the air; (*2*) by treating MnO_2 with concentrated H_2SO_4 at a temperature of about 130°, forming $Mn_2(SO_4)_3$ and then adding water: $Mn_2(SO_4)_3 + 4H_2O = 2MnO(OH) + 3H_2SO_4$ (Carius, *A.*, 1856, **98**, 63). (*c*) **Trimanganese tetroxide, Mn_3O_4**, is formed when any of the higher or lower oxides of manganese or any manganese salts with a volatile acid are heated in the air to a white heat (Wright and Luff, *B.*, 1878, **11**, 2145). The corresponding hydroxide would be $Mn_3(OH)_8$; this has not been isolated. A corresponding oxide-hydroxide is formed by adding freshly formed and moist MnO_2 to an excess of $MnCl_2$ containing NH_4Cl (Otto, *A.*, 1855, **93**, 372).

(*d*) Manganese peroxide, MnO_2, is formed (*1*) by heating $Mn(NO_3)_2$ to 200° (Gorgeu, *C. r.*, 1879, 88, 796); (*2*) by heating $MnCO_3$ with $KClO_3$ to 300°; (*3*) by boiling any manganous salt with concentrated HNO_3 and $KClO_3$. A corresponding hydroxide, $Mn(OH)_4$, has not been isolated. Several other hydroxides, *e. g.*, $MnO(OH)_2$, $Mn_2O_3(OH)_2$, $Mn_3O_4(OH)_4$ etc., have been produced. The chief use of manganese dioxide is in the preparation of chlorine or bromine. (*e*) **Manganates.**—*Manganic* acid, H_2MnO_4, is not known in a free state. The corresponding salt, K_2MnO_4, is formed when any form of manganese is fused with KOH or K_2CO_3 (*1*) in the air, oxygen being absorbed; or (*2*) with KNO_3 or $KClO_3$, NO or KCl being formed. A manganate of the alkali metals is soluble in water, *with gradual decomposition* into manganese dioxide and permanganates: $3K_2MnO_4 + 2H_2O = 2KMnO_4 + MnO_2 + 4KOH$. Free alkali retards, and free acids and boiling promote, this change. Manganates have a green *color*, which turns to the red of permanganates during the decomposition inevitable in solution. This is the usual method of manufacturing $KMnO_4$. (*f*) **Permanganic acid** is not in use as an acid, but is represented by the permanganates, as $KMnO_4$. The permanganic acid radical is at once decomposed by addition of hot H_2SO_4 to a solid permanganate (*1*), but in water solution this decomposition does not at once take place, except by contact with oxidizable substances. The oxidizing power of permanganates extends to a great number of substances, possesses different characteristics in acid and in alkaline solutions, and acts in many cases so rapidly as to be violently explosive. The reactions with ferrous salts (*2*) and with oxalic acid (*3*) are much used in volumetric analysis.

(*1*) $4KMnO_4 + 2H_2SO_4 = 2K_2SO_4 + 4MnO_2 + 3O_2 + 2H_2O$

and $2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2$

or $4KMnO_4 + 6H_2SO_4 = 4MnSO_4 + 2K_2SO_4 + 5O_2 + 6H_2O$

(*2*) $KMnO_4 + 5FeCl_2 + 8HCl = MnCl_2 + KCl + 5FeCl_3 + 4H_2O$

(*3*) $2KMnO_4 + 5H_2C_2O_4 + 6HCl = 2MnCl_2 + 2KCl + 8H_2O + 10CO_2$

5. **Solubilities.**—*a.*—*Metal.*—Manganese dissolves readily in dilute acids to form manganous salts. Concentrated H_2SO_4 dissolves it only on warming, SO_2 being evolved. It combines readily with chlorine and bromine. *b.*—*Oxides* and *hydroxides.*—All oxides and hydroxides of manganese are insoluble in water. They are soluble, upon warming, in hydrochloric acid, forming manganous chloride; the higher oxides and hydroxides being reduced with evolution of chlorine (commercial method of preparation of chlorine). Instead of hydrochloric acid, sulphuric acid and a chloride may be employed (HBr and HI act similarly to, and more readily than HCl). In the cold, hydrochloric acid dissolves MnO_2 to a greenish-brown solution, containing, probably, $MnCl_3$ or $MnCl_4$, unstable, giving chlorine when warmed and forming MnO_2 when strongly diluted with water (Pickering, *J. C.*, 1879, 35, 654; Nickles, *A. Ch.*, 1865, (4), 5, 161). Nitric and sulphuric acids dissolve manganous oxide and hydroxide to manganous salts. Manganese dioxide (or hydrated oxide) is insoluble in nitric acid, dilute or concentrated; concentrated sulphuric acid with heat decomposes it, evolving oxygen and forming manganous sulphate: $2MnO_2 + 2H_2SO_4 = 2MnSO_4 + 2H_2O + O_2$. Manganous hydroxide is insoluble in the alkalis but *soluble* in solutions of *ammonium salts.*

c.—*Salts.*—Manganous sulphide, carbonate, phosphate, oxalate, borate, and sulphite are insoluble in water, readily soluble in dilute acids. **Manganic salts** are somewhat unstable compounds, of a reddish-brown or purple-red *color*, becoming paler and of lighter tint on reduction to the manganous combination. $MnCl_2$ and $MnSO_4$ are *deliquescent*. Manganic *chloride*, $MnCl_3$, and the *perchloride*, $MnCl_4$, are unstable salts which

are decomposed by water especially when hot, to $MnCl_2$ and *chlorine*. The *trichloride* is greenish black, soluble in absolute alcohol and ether; while the *tetrachloride* is reddish-brown soluble in absolute alcohol. (W. B. Holmes, *J. Am. Soc.* **29**, 1277.) Manganic *sulphate* $Mn_2(SO_4)_3$, is soluble in dilute sulphuric acid, but is reduced to $MnSO_4$ by the attempt to dissolve it in water alone; potassium manganic sulphate and other *manganic alums* are also decomposed by water. Alkali *manganates* and *permanganates* are soluble in water, the former rapidly changing to manganese dioxide and permanganate, which is much more stable in solution. In presence of reducing agents both manganates and permanganates are reduced to lower forms.

$$K_2MnO_4 + 8HCl = MnCl_2 + 2KCl + 2Cl_2 + 4H_2O$$
$$2KMnO_4 + 3MnSO_4 + 2H_2O = 5MnO_2 + K_2SO_4 + 2H_2SO_4$$

Concentrated H_2SO_4 in the cold dissolves $KMnO_4$, forming $(MnO_3)_2SO_4$ (a sulphate of the heptad manganese: $2KMnO_4 + 3H_2SO_4 = (MnO_3)_2SO_4 + 2KHSO_4 + 2H_2O$ (Franke, *J. pr.*, 1887, **36**, 31). If heat be applied oxygen is evolved and the manganese is reduced to the dyad (4*f*).

6. **Reactions.** *a*.—The **fixed alkali hydroxides** precipitate from solutions of manganous salts, *manganous hydroxide*, $Mn(OH)_2$, white, soon turning brown in the air by oxidation to manganic hydroxide, $MnO(OH)$. The precipitate is formed by the reaction of the negative hydroxyl ion of the alkali with the positive manganous ion:

$$2\overset{+}{N}H_4\ \overset{-}{O}H + \overset{++}{Mn}\ \overset{--}{Cl_2} = Mn(OH)_2 + 2\overset{+}{N}H_4\ \overset{-}{Cl}.$$

The precipitate is insoluble in excess of the alkalis because the manganous or manganic manganese does not form an acid ion. Before the manganous manganese is oxidized it is soluble in excess of ammonium salts because a complex salt is formed in which the manganese forms a part of the acid ion:

$$Mn(OH)_2 + 4\overset{+}{N}H_4\ \overset{-}{Cl} = (\overset{+}{N}H_4)_2\ \overset{--}{MnCl_4} + 2\overset{+}{N}H_4\overset{-}{Cl}.$$

(*1*). **Ammonium hydroxide** precipitates one-half of the manganese as the hydroxide from solutions of manganous salts, the other half being held in solution as an acid ion by the ammonium salt formed (*2*) (*Dammer*, **3**, 237). The presence of excess of ammonium salt prevents the precipitation of the manganese by ammonium hydroxide because the manganese is present in the acid ion (*3*) (separation of manganese from the metals of the third group) (Pickering, *J. C.*, 1879, **35**, 672; Langbein, *Z.*, 1887, **26**, 731). *Manganic hydroxide*, $MnO(OH)$, is insoluble in the alkalis or in ammonium salts. It gradually precipitates, completely on exposure to the air, as a dark brown precipitate from solutions

of manganous hydroxide in ammonium salts. Alkali **carbonates** precipitate *manganous carbonate*, $MnCO_3$, white, oxidized in the air to the brown manganic hydroxide, and before oxidation, somewhat soluble in ammonium chloride. Strong ammonium hydroxide gradually reduces a solution of potassium permanganate to manganese dioxide (10*b*).

(*1*) $Mn(OH)_2 + 4NH_4Cl = (NH_4)_2MnCl_4 + 2NH_4OH$
(*2*) $2MnSO_4 + 2NH_4OH = (NH_4)_2Mn(SO_4)_2 + Mn(OH)_2$
(*3*) $MnCl_2 + 2NH_4Cl = (NH_4)_2MnCl_4$

b.—**Oxalic acid** and alkaline **oxalates** precipitate *manganous oxalate*, soluble in mineral acids not too dilute. All compounds of manganese of a higher degree of oxidation are reduced to the manganous condition on warming with *oxalic acid*, or *oxalates* in presence of some mineral acid: $2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$.

Soluble **cyanides**, as **KCN**, precipitate *manganous cyanide*, $Mn(CN)_2$, white, but darkening in the air; soluble in excess of the precipitant by formation of double cyanides, as $Mn(CN)_2.2KCN$. This solution, exposed to the air, produces *manganicyanides* (analogous to ferricyanides), with oxidation of the manganese: $12(Mn(CN)_2.2KCN) + 3O_2 + 2H_2O = 8K_3Mn(CN)_6 + 4MnO(OH)$. Fe''' and Mn'' may be separated by treating a solution of the two metals with a strong excess of **KCN** and then with iodine. The manganese is precipitated as MnO_2 and the iron remains in solution (Beilstein and Jawein, *B.*, 1879, **12**, 1528). **Ferrocyanides** precipitate white *manganous ferrocyanide*, $Mn_2Fe(CN)_6$, soluble in hydrochloric acid. **Ferricyanides** precipitate brown *manganous ferricyanide*, $Mn_3(Fe(CN)_6)_2$, insoluble in acids (separation, with **Co** and **Ni**, from **Zn**) (Tarugi, *Gazzetta*, 1895, **25**, ii, 478). If an alkali or alkali carbonate be present, potassium ferricyanide oxidizes manganous compounds to manganese dioxide, the ferricyanide being reduced to ferrocyanide. Potassium ferrocyanide reduces manganates and permanganates to manganous compounds.

c.—**Nitric acid** is of value in analysis of manganese compounds in that it, as a non-reducing acid, acts readily with oxidizing agents, as PbO_2, $KClO_3$, etc., to oxidize manganous compounds to manganese dioxide or to permanganic acid. Reducing agents as **HCl**, etc., should be absent. Sulphuric acid may be used instead of nitric acid.

$2Mn(NO_3)_2 + 5PbO_2 + 6HNO_3 = 2HMnO_4 + 5Pb(NO_3)_2 + 2H_2O$
$5MnSO_4 + 2KClO_3 + H_2SO_4 + 4H_2O = 5MnO_2 + K_2SO_4 + Cl_2 + 5H_2SO_4$

In using PbO_2 and HNO_3 to detect manganese, the compound should first be reduced with hydrochloric acid, precipitated with potassium hydroxide and this precipitate dissolved in nitric acid, as MnO_2 is not all oxidized by PbO_2 and HNO_3 (Koninck, *Z. angew.*, 1889, 4).

d.—**Hypophosphorous acid** reduces all higher forms of manganese to the manganous condition. Alkali **phosphates**, as Na_2HPO_4, precipitate, from neutral solutions of manganous salts, normal *manganous phosphate*, $Mn_3(PO_4)_2$, white, slightly soluble in water, and soluble in dilute acids. It turns brown in the air. The manganous hydrogen phosphate, $MnHPO_4$, is more soluble in water, and is obtained by crystallization from a mixture of manganous sul-

phate acidulated with acetic acid and disodium phosphate, Na_2HPO_4, added till a precipitate begins to form. From the ammonium-manganese solution, freshly formed (6*a*), phosphates precipitate all the manganese as *manganous ammonium phosphate.*

e.—**Hydrosulphuric acid** precipitates manganous acetate but imperfectly, and not in presence of acetic acid, and does not precipitate other salts, as manganous sulphide is soluble in very dilute acids, even acetic acid. **Ammonium sulphide** precipitates from neutral solutions, and forms from the recent hydroxide of mixtures made alkaline, the flesh-colored *manganous sulphide*, **MnS**. Acetic acid, acting on the precipitated sulphides, separates manganese from cobalt and nickel, and from the greater part of zinc. All the higher oxidized forms of manganese (in solution or freshly precipitated) are reduced to the manganous condition, with separation of sulphur (10), by hydrosulphuric acid or soluble sulphides: $4KMnO_4 + 14(NH_4)_2S + 16H_2O = 4MnS + 4KOH + 28NH_4OH + 5S_2$. The *green manganous sulphide*, **MnS**, crystalline, anhydrous, is formed by the action of H_2S on a hot ammoniacal manganous solution not containing an excess of ammonium salts (Meineke, *Z. angew.*, 1888, 3), also by pouring the neutral manganous solution into a hot solution of ammonium chloride and excess of colorless ammonium sulphide. The fixed alkali sulphides produce a red manganous sulphide.

Soluble Sulphites precipitate from solutions of manganous salts, manganous sulphite, $MnSO_3$, white, insoluble in water, soluble in acids (Gorgeu, *C. r.*, 1883, **96**, 341). Solutions of manganates or permanganates are immediately reduced to the flocculent brown-black manganese dioxide by solutions of **sodium sulphite** or **sodium thiosulphate;** if acids be present, the reduction is complete to manganous salts.

f.—**HCl**, **HBr**, and **HI** readily reduce the higher compounds of manganese to manganous salts with evolution of the corresponding halogen. When manganese dioxide is dissolved in concentrated **HCl** without heat, the dark brownish colored solution contains manganese tetrachloride, $MnCl_4$, and trichloride, $MnCl_3$ which deposits MnO_2 on dilution with water and on warming decomposes into manganous chloride and chlorine (5*b*) (Pickering, *J. C.*, 1879, **35**, 654, W. B. Holmes, *J. Am. Soc.* **29**, 1277). Potassium iodide instantly reduces a solution of potassium permanganate, forming manganese dioxide and an iodate (distinction from chloride and bromide). Potassium **chlorate** or **bromate** when boiled with concentrated nitric or sulphuric acids and manganous compounds forms manganese dioxide (*c*).

g.—Soluble **arsenites** precipitate *manganous arsenite*, and **arsenates** precipitate *manganous arsenate*, insoluble in water, soluble in acids. **Arsenous acid** and **arsenites** reduce solutions of manganates or permanganates, forming a brown **flocculent precipitate;** or a colorless solution if warmed in presence of a mineral acid. *h.*—**Normal potassium chromate** precipitates manganous salts, brown, soluble in acids and in ammonium hydroxide; no precipitate is formed with potassium dichromate. *i.*—Soluble **manganates** and **permanganates** pre-

cipitate manganous salts as manganese dioxide, being themselves reduced to the same form: $3MnSO_4 + 2KMnO_4 + 2H_2O = 5MnO_2 + K_2SO_4 + 2H_2SO_4$.

7. **Ignition with alkali** and **oxidizing agents,** forming a *bright green* mass of alkaline *manganate*, constitutes a delicate and convenient test for manganese, in any combination. A small portion of precipitate or fine powder is taken. If the manganese forms but a small part of a mixture to be tested, it is better to submit the substance to the systematic course of analysis, and apply this test to the precipitate by alkali, in the fourth group. A convenient form of the test is by **ignition on platinum foil with potassium** or sodium **nitrate** and sodium carbonate (*a*). Ignition, by an **oxidizing flame,** on platinum foil, with potassium hydroxide, effects the same result, less quickly and perfectly (*b*). Ignition by the oxidizing flame of the blow-pipe, in a **bead of sodium carbonate,** on the loop of platinum wire, also gives the green color (*c*).

(*a*) $Mn(OH)_2 + 2KNO_3 + Na_2CO_3 = Na_2MnO_4 + 2KNO_2 + CO_2 + H_2O$

or if a small amount of KNO_3 is present,

(*b*) $3Mn(OH)_3 + 4KNO_3 + Na_2CO_3 = 2K_2MnO_4 + Na_2MnO_4 + 4NO + CO_2 + 3H_2O$

(*c*) $Mn(OH)_2 + 2KOH + O_2 = K_2MnO_4 + 2H_2O$

(*d*) $Mn(OH)_2 + Na_2CO_3 + O_2 = Na_2MnO_4 + H_2O + CO_2$

With **beads of borax** and **microcosmic salt,** before the outer blow-pipe flame, manganese colors the bead violet while hot, and *amethyst-red* when cold. The color is due to the formation of *manganic oxide*, the coloring material of the amethyst and other minerals, and is slowly destroyed by application of the inner flame, which reduces the manganic to manganous oxide.

8. **Detection.**—After the removal of the metals of the first three groups (the third group in the presence of NH_4Cl in excess, 5*b* and 6*a*), the **Mn** with **Co**, **Ni** and **Zn** is precipitated in the ammoniacal solution by H_2S. By digestion in cold dilute **HCl** the sulphides of **Mn** and **Zn** are dissolved, and after boiling to remove the H_2S, **Mn** is precipitated as the hydroxide by excess of **KOH**, which dissolves the **Zn**. The precipitate of the manganese is dissolved in HNO_3 and boiled with more HNO_3 and an excess of PbO_2. A violet-colored solution is evidence of the presence of manganese.

9. **Estimation.**—(*1*) By converting into Mn_3O_4 (4*c*), and weighing as such. (*2*) By precipitating as $MnNH_4PO_4$, and after ignition weighing as $Mn_2P_2O_7$. (*3*) By treating the neutral manganous salt with a solution of $KMnO_4$ of known strength (6*i*). If some $ZnSO_4$ is added the action is more satisfactory (Wright and Menke, *J. C.*, 1880, **37**, 42). (*4*) By boiling the manganous compound with PbO_2 and HNO_3, and comparing the color with a permanganate solution of known strength (Peters, *C. N.*, 1876, **33**, 35). (*5*) The manganous compound is oxidized to MnO_2 by boiling with $KClO_3$ and HNO_3. This is then reduced by an excess of standard H_2O_2, $H_2C_2O_4$, or $FeSO_4$, and the excess of the reagent estimated by the usual methods. (*6*) MnO_2, obtained as in (*5*), is treated with $H_2C_2O_4$ and the evolved CO_2 measured or weighed. (*7*) MnO_2, obtained as in (*5*), is boiled with **HCl** and the evolved **Cl** estimated.

10. **Oxidation.**—(*a*) Mn'' is oxidized to Mn''' in alkaline mixture on exposure to the air; to Mn^{IV} in neutral solution by K_2MnO_4 and $KMnO_4$,

in alkaline mixture by Cl, Br, I, $K_3Fe(CN)_6$, $KClO$, $KBrO$, H_2O_2[1], etc.; in acid solution by boiling with concentrated HNO_3 or H_2SO_4, and $KClO_3$ or $KBrO_3$. Mn^{VI-n} is oxidized to Mn^{VI} by fusion with an alkali and an oxidizing agent, or by fusion with $KClO_3$ alone (Boettger, *Z.*, 1872, **11**, 433). Mn^{VII-n} is oxidized to Mn^{VII} by warming with PbO_2 or Pb_3O_4 and HNO_3 or H_2SO_4. The higher oxide of lead should be in excess and reducing agents should be absent as they delay the reaction; hence in analysis the manganese should be precipitated as the hydroxide or sulphide, filtered, washed, and then dissolved in HNO_3 or H_2SO_4, and boiled with the higher oxide of lead (6*c*). A solution of potassium manganate decomposes into potassium permanganate and manganese dioxide on standing, more rapidly on warming or dilution with water. (*b*) All compounds of manganese having a higher degree of oxidation than the dyad, (Mn''^{+n}) are reduced to the dyad (Mn'') by $H_2C_2O_4$, HH_2PO_2, H_2S[4], K_2S, H_2SO_3, H_2O_2[2] (in neutral or alkaline solution to Mn^{IV}), HCl, HBr, HI, $HCNS$, Hg', Sn'', As''', Sb''', Cu', Fe'', Cr'', Cr''', etc.; the reducing agents becoming respectively CO_2, P^V, $S°$ to S^{VI} (depending upon the temperature, concentration, and the agent used in excess), Cl, Br, I, HCN and S^{VI}, Hg'', Sn^{IV}, As^V, Sb^V, Cu'', Fe''', and Cr^{VI}. Mn^{IV+n} is reduced to Mn^{IV} (or Mn''') by H[3], AsH_3[3], SbH_3[3], PH_3[3], Na_2SO_3[4], $Na_2S_2O_3$[4], NH_4OH[3] (slowly), Mn'', etc. $KMnO_4$ is reduced to K_2MnO_4 on boiling with concentrated KOH: $4KMnO_4 + 4KOH = 4K_2MnO_4 + 2H_2O + O_2$ (Rammelsberg, *B.*, 1875, **8**, 232).

§135. Zinc. $Zn = 65.37$. Valence two.

1. **Properties.**—*Specific gravity*, 7.142 (Spring, *B.*, 1883, **16**, 2723). *Melting point*, 418.5° to 419.35° (Burgess, *Wash. Acad. of Sci.*, 1–18). *Boiling point*, 918° (Berthelot, *C. r.*, 1912, 134). It is a bluish-white metal, retaining its lustre in dry air, but slightly tarnished in moist air or in water. When heated to the boiling point with abundant excess of air it burns with a bluish-white flame to zinc oxide. Zinc dust mixed with sulphur is ignited by percussion (Schwarz, *B.*, 1882, **15**, 2505). At ordinary temperature it breaks with a coarse crystalline fracture. It is more malleable at 100° to 150° than at other temperatures, and at that temperature may be drawn into wire or rolled into sheets. At 205° it is so brittle that it may be easily powdered in a mortar.

Zinc finds an extended use in laboratories for the generation of hydrogen. It is molded in sticks or granulated by pouring the molten metal into cold water. The pure metal is not suitable for the generation of hydrogen, as the reaction with acids proceeds too slowly (Weeren, *B.*, 1891, **24**, 1785). Commercial impurities render the metal readily soluble in acids, or the pure metal may be treated with a dilute solution of platinum chloride (twenty milligrams $PtCl_4$ per litre), or copper sulphate. Metallic platinum or copper is deposited upon the zinc: $PtCl_4 + 2Zn = Pt + 2ZnCl_2$, $CuSO_4 + Zn = Cu + ZnSO_4$.

2. **Occurrence.**—It is found as calamine ($ZnCO_3$), as zinc-blende (ZnS); also associated with other metals in numerous ores.

3. **Preparation.**—The process usually employed consists of two operations:

[1] Klein, *Arch. Pharm.*, 1880, **227**, 77; Jannaesch and von Cloedt, *Z. anorg.*, 1895, **10**, 398 and 410; Carnot, *C. r.*, 1888, **107**, 997 and 1150.

[2] Carnot, Bl., 1889, (3), **1**, 277; Gorgeu, *C. r.*, 1890, **110**, 958. [3] Jones, *J. C.*, 1878, **33**, 96. [4] Hoenig and Zatzek, *M.*, 1883, **4**, 738; Glaeser, *M.*, 1885, **6**, 329.

(*1*) Roasting: in case of the carbonate the action is: $ZnCO_3 = ZnO + CO_2$; if it is a sulphide, $2ZnS + 3O_2 = 2ZnO + 2SO_2$. (*2*) Reduction with distillation; after mixing the **ZnO** with one-half its weight of powdered coal, it is distilled at a white heat. Its usual impurities are **As**, **Cd**, **Pb**, **Cu**, **Fe** and **Sn**. It is purified by repeated distillation, each time rejecting the first portion, which contains the more volatile **As** and **Cd**, and the last which contains the less volatile **Pb**, **Cu**, **Fe** and **Sn**. Strictly chemically pure zinc is best prepared from the carbonate which has been purified by precipitation.

4. **Oxide** and **Hydroxide.**—Zinc oxide (**ZnO**) is made by igniting in the air either metallic zinc, its hydroxide, carbonate, nitrate, oxalate, or any of its organic oxysalts. Zinc hydroxide, $Zn(OH)_2$, is made from solutions of zinc salts by precipitation with fixed alkalis (*6a*).

5. **Solubilities.**—(*a*) *Metal.*—Pure zinc dissolves very slowly in acids or alkalis, unless in contact with copper, platinum or some less positive metal (Baker, *J. C.*, 1885, **47**, 349). The metallic impurities in ordinary zinc enable it to dissolve easily with acids or alkali hydroxides. In contact with iron, it is quite rapidly oxidized in water containing air, but not dissolved by water unless by aid of certain salts. It dissolves in dilute hydrochloric, sulphuric * and acetic acids (*1*), and in the aqueous alkalis (*2*), with evolution of hydrogen; in very dilute nitric acid, without evolution of gas (*3*); in moderately dilute cold nitric acid, mostly with evolution of nitrous oxide (*4*); and, in somewhat less dilute nitric acid, chiefly with evolution of nitric oxide (*5*). Concentrated nitric acid dissolves zinc but slightly, the nitrate being very sparingly soluble in nitric acid (Montemartini, *Gazzetta*, 1892, **22**, 277). Hot concentrated sulphuric acid dissolves it with evolution of sulphur dioxide (*6*).

(*1*) $Zn + H_2SO_4 = ZnSO_4 + H_2$

(*2*) $Zn + 2KOH = K_2ZnO_2 + H_2$

(*3*) $4Zn + 10HNO_3 = 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$

(*4*) $4Zn + 10HNO_3 = 4Zn(NO_3)_2 + N_2O + 5H_2O$

(*5*) $3Zn + 8HNO_3 = 3Zn(NO_3)_2 + 2NO + 4H_2O$

(*6*) $Zn + 2H_2SO_4 = ZnSO_4 + SO_2 + 2H_2O$

(*b*) *Oxide* and *Hydroxide.*—All the agents which dissolve the metal, dissolve also its oxide and hydroxide.

(*c*) *Salts.*—The chloride, bromide, iodide, chlorate, nitrate (6aq), and acetate (7aq) are *deliquescent:* the sulphate (7aq) is efflorescent. The chloride is readily soluble in alcohol in all proportions (Kremers, *Pogg.*, 1862, **115**, 360). The sulphide, basic carbonate, phosphate, arsenate, oxalate, and ferrocyanide are insoluble in water; the sulphite is sparingly soluble. The ferrocyanide is insoluble in hydrochloric acid (Fahlberg, *Z.*, 1874, **13**, 380). The sulphide is almost insoluble in dilute acetic acid (separation from **MnS**). All zinc salts are soluble in **KOH** and **NaOH** except zinc sulphide, and all in NH_4OH except **ZnS** and $Zn_2Fe(CN)_6$.

6. **Reactions.** *a.*—The **fixed alkali hydroxides** precipitate *zinc hydroxide*, $Zn(OH)_2$, white, soluble in excess of the precipitant forming an *alkali zincate:*

$$ZnCl_2 + 2KOH = Zn(OH)_2 + 2KCl$$
$$Zn(OH)_2 + 2KOH = K_2ZnO_2 + 2H_2O$$

Ammonia precipitates from neutral solutions free from ammonium salts, zinc hydroxide, soluble in excess of ammonia or ammonium salts forming complex zinc ammonia ions:

$$ZnCl_2 + 2NH_4OH = Zn(OH)_2 + 2NH_4Cl$$
$$Zn(OH)_2 + 6NH_3 = Zn(NH_3)_6(OH)_2$$

* Muir and Robbs, *C. N.*, 1882, **45**, 69.

The precipitate of zinc hydroxide dissolves more readily in excess of the alkalis at ordinary temperature than when heated. Unless a strong excess of the alkali be present, boiling causes a precipitation of zinc oxide, more readily from the solution in ammonium hydroxide than in the fixed alkalis. The presence of other metals—as iron or manganese—makes necessary the use of much more alkali to effect solution. An alkali solution as dilute as tenth Normal does not dissolve zinc hydroxide, no matter how great an excess be added (Prescott, *J. Am. Soc.*, 1880, **2**, 29).

Alkali carbonates precipitate the basic carbonate, $Zn_5(OH)_6(CO_3)_2$, white, soluble in ammonium carbonate, readily in alkali hydroxides (Kraut, *Z. anorg.*, 1896, **13**, 1). Carbonates of **Ba**, **Sr**, **Ca**, and **Mg** have no action at ordinary temperatures (separation from **Fe'''**, **Al**, and **Cr'''**), but upon boiling precipitate the whole of the zinc.

b.—Alkali **cyanides**, as **KCN**, precipitate zinc cyanide, $Zn(CN)_2$, white, soluble in excess of the precipitant. Alkali **ferrocyanides**, as $K_4Fe(CN)_6$, precipitate zinc ferrocyanide, $Zn_2Fe(CN)_6$, white (5*c*). Alkali **ferricyanides**, as $K_3Fe(CN)_6$, precipitate zinc ferricyanide, $Zn_3(Fe(CN)_6)_2$, yellowish. *c.*—See 5*c*. *d.*—**Sodium phosphate**, Na_2HPO_4, precipitates *zinc phosphate*, soluble in alkali hydroxides and in nearly all acids.

e.—**Hydrosulphuric** acid precipitates a part of the zinc from neutral solutions of its salts with mineral acids, and the whole from the acetate; also from other salts of zinc, by addition of alkali acetates or monochloracetic acid, in small excess (separation from **Mn**, **Co**, **Ni**, and **Fe**) (Berg, *Z.*, 1886, **25**, 512): $ZnCl_2 + 2KC_2H_3O_2 + H_2S = ZnS + 2KCl + 2HC_2H_3O_2$.* That is: Zinc sulphide is not entirely soluble in dilute acids, though much more soluble in mineral acids than in acetic acid. The precipitate is white when pure. **Alkali sulphides** completely precipitate zinc as *sulphide*, both from its salts with acids and from its soluble combinations with alkalis.

Concentrated solutions of **sodium sulphite** precipitate solutions of zinc salts as basic zinc sulphite; or if the solutions be too dilute for immediate precipitation, boiling will cause the immediate formation of the bulky white precipitate of the basic sulphite (Seubert, *Arch. Pharm.*, 1891, **229**, 316). *f.*—If a hot concentrated zinc chloride solution be treated with ammonium hydroxide until a precipitate begins to form, a basic chloride, $2ZnCl_2.9ZnO$, will separate out upon cooling as a white precipitate (Habermann, *M.*, 1884, **5**, 432).

g.—Zinc salts are precipitated by solutions of alkali **arsenites** and **arsenates**, forming respectively zinc arsenite or arsenate, white, gelatinous, readily soluble in alkalis and acids, including arsenic acids. *h.*—Normal potassium **chro-**

*In the equation for acetic acid, $ab = kc$, **a** and **b**, the concentrations of the **H** and $C_2H_3O_2$ ions respectively, are small, **c** is large, and **k**, the so-called "dissociation-constant," to which the strength of the acid is proportional, is very small. But addition of the fully-dissociated sodium acetate to the likewise completely-ionized hydrochloric acid gives a solution containing the ions in very large concentration and practically none of the non-dissociated acetic acid. To restore equilibrium the **H** ions of the **HCl** unite with the acetic ions of the sodium acetate, leaving **Na** and **Cl** ions in the solution. The displacement of a weak acid from its salt by a strong one lies then not so much in an attraction of the strong acid by the base as in the tendency of the weak acid to form the non-ionized molecule.

mate forms, with solutions of zinc salts, a yellow precipitate readily soluble in alkalis and acids, including chromic acid. No precipitate is formed with $K_2Cr_2O_7$.

7. **Ignition.**—With sodium carbonate, on charcoal, before the blow-pipe, compounds of zinc are reduced to the metallic state. The metal is vaporized, and then oxidized in the air, and deposited as a non-volatile coating, yellow when hot and white when cold. If this coating, or zinc oxide otherwise prepared, be moistened with solution of cobalt nitrate and again ignited, it assumes a green color (Bloxam, *J. C.*, 1865, **18**, 98). With borax or microcosmic salt, zinc compounds give a bead which, if strongly saturated, is yellowish when hot, and opaque white when cold.

8. **Detection.**—After the removal of the first three groups, the **Zn** is precipitated with **Co**, **Ni** and **Mn** from the ammoniacal solutions by H_2S. Digestion of the precipitated sulphides with cold dilute **HCl** dissolves the **Mn** and **Zn** as chlorides. The solution is thoroughly boiled to expel the H_2S and the zinc changed to Na_2ZnO_2 by an excess of **NaOH**, which precipitates the manganese as the hydroxide. From the alkaline filtrate H_2S gives a white or grayish-white precipitate—evidence of the presence of **Zn**.

9. **Estimation.**—(*1*) Zinc is weighed as an oxide, into which form it is brought by simple ignition if combined with a volatile inorganic oxyacid, otherwise it should be changed to a carbonate and then ignited. (*2*) It is converted into a sulphide, and after adding powdered sulphur it is ignited in a stream of hydrogen or hydrogen sulphide, and weighed as a sulphide (Künzel, *Z.*, 1863, **2**, 373). (*3*) It may be converted into $ZnNH_4PO_4$, and, after drying at 100°, weighed. Ignition converts it into $Zn_2P_2O_7$, with slight loss of zinc. (*4*) Volumetrically, by converting into $Zn_2Fe(CN)_6$ and titrating with potassium permanganate or by using $FeCl_3$ acidulated with $HC_2H_3O_2$ as external indicator (Voigt, *Z. angew*, 1889, 307). (*5*) By precipitation as $Zn_3(Fe(CN)_6)_2$, treating the precipitate with potassium iodide and titrating the liberated iodine (Mohr, *Dingl.*, 1858, **48**, 115). (*6*) By titration in hydrochloric acid solution with $K_4Fe(CN)_6$, using a uranium salt as an indicator (Fahlberg, *Z.*, 1874, **13**, 379; Koninck and Prost, *Z. angew.*, 1896, 568). (*7*) By titration in alkaline solution with Na_2S, using a copper salt as an indicator. (*8*) The zinc is precipitated as $ZnNH_4AsO_4$, the precipitate decomposed with **HI** and the liberated iodine titrated with standard $Na_2S_2O_3$ (Meade, *J. Am. Soc.*, 1900, **22**, 353).

10. **Oxidation.**—Metallic zinc precipitates the free metal from solutions of **Cd**, **Sn**, **Pb**, **Cu**, **Bi**, **Hg**, **Ag**, **Pt**, **Au**, **As**, **Sb**, **Te**, **In**, **Fe**[1], **Co**, **Ni**, **Pd**, **Rh**, **Ir**, and **Os** (Gmelin-Kraut, *Handbuch*, 1875, **3**, 6). Zinc with copper (zinc-copper couple, used in water analysis) reduces nitrates and nitrites to ammonia, chlorates to chlorides, iodates to iodides, ferricyanides to ferrocyanides, etc. (Thorpe, *J. C.*, 1873, **26**, 541). Solutions of chromates are reduced to chromic salts, ferric salts to ferrous salts, and compounds of manganese having more than two bonds are reduced to the dyad in presence of some non-reducing acid. Zinc is precipitated as the metal from acetic solutions by **Mg** (Warren, *C. N.*, 1895, **71**, 92). The oxide is reduced to the metal by heating in a current of hydrogen (Deville, *A. Ch.*, 1855 (3), **43**, 477).

[1] Davies, *J. C.*, 1875, **28**, 311.

§136. Comparison of some Reactions of the Iron and Zinc Group Bases.

In Water Solution, as Chlorides, Nitrates, Sulphates, etc.

	Aluminum.	Chromium.* Cr'''	Ferricum. Fe'''	Ferrosum. Fe''	Manganese. Mn''	Cobalt. Co''	Nickel. Ni''.	Zinc.
KOH or NaOH	$Al(OH)_3$ †	$Cr(OH)_3$ ‡	$Fe(OH)_3$	$Fe(OH)_2$	$Mn(OH)_2$	$Co(OH)_2$	$Ni(OH)_2$	$Zn(OH)_2$ †
NH_4OH	"	"	"	"	"	" ¶	" ¶	" ¶
NH_4OH with NH_4Cl	"	"	"	Partial pre.	No pre.	No pre.	No pre.	No pre.
Carbonates	"	"	"	$FeCO_3$	$MnCO_3$	Basic carb.	Basic carb.	Basic carb.
Sulphides	"	"	FeS with S	FeS	MnS	CoS	NiS	ZnS
H_2S in acid solution	No pre.	No pre.	S **	No pre.	No pre. ***	.... ††	.... ††	.... ††
Na_2HPO_4	$AlPO_4$ ‡‡	$CrPO_4$ ‡‡	$FePO_4$ ‡‡	$FeHPO_4$ and $Fe_3(PO_4)_2$	$Mn_3(PO_4)_2$	$CoHPO_4$	$NiHPO_4$	$ZnHPO_4$
Nitroso-β-naphthol§ in hot acid sol.	No pre.	No pre.	Black pre.	Black pre.	No pre	Brick red precipitate	No pre.	No pre.
Certain oxidizing agents	....	Base to acid	....	To ferric	Base to acid	Cobaltic	Nickelic	....
Certain reducing agents	....	Acid to base	To Ferrous	....	Acid to base	....	....	....

* Chromic acid and its salts furnish Cr''' as a base when treated with ammonium sulphide, hydrogen sulphide, and other reducing agents (§125, 6e and 10).

† The precipitates soluble in excess of the reagent (§124, 6a; §135, 6a).

‡ The precipitate soluble in excess of the cold reagent, but thrown down again on boiling (§125, 6a).

¶ The precipitates soluble in excess of the reagent (§132, 6a; §133, 6a; §135, 6a).

** The color fades, with precipitate of sulphur and reduction to ferrous salt (§126, 6e).

†† In solutions of normal acetates, hydrogen sulphide gives precipitates (§132, 6e; §133, 6e; §135, 6e).

‡‡ Much less soluble in acetic acid than alkaline-earth phosphates (§126, 6d).

*** In case manganese is present as $KMnO_4$ its occurrence in the second and third groups should always be prevented by previous reduction to a manganous salt by boiling with hydrochloric acid until the color disappears (§134, 6f).

§ A valuable reagent for the separation of cobalt from nickel (§132, 6b).

§137. Table for Analysis of the Zinc Group (Fourth Group)

(Phosphates and Oxalates being absent).

Into the clear **ammoniacal filtrate** from the **Third Group** pass *Hydrogen Sulphide*, and if a precipitate appears, **warm** until it subsides. Filter and wash with a one per cent solution of NH_4Cl. (Test filtrate, in which H_2S gives no precipitate for the **Fifth Group**.)

Precipitate: CoS, NiS, MnS, ZnS.

Treat on the filter with *cold* dilute **Hydrochloric Acid** (1–4).

Residue: CoS, NiS * (black).

Test with the borax bead. A blue bead indicates cobalt, (§132, 7).

Dissolve the remainder of the sulphides in nitro-hydrochloric acid or **HCl** + crystal of $KClO_3$. Evaporate to expel excess of Cl_2, neutralize with NH_4OH and divide into two parts.

For **Cobalt:**	For **Nickel:**
Add $NaHCO_3$ and H_2O_2; warm gently and filter. A green color to the filtrate indicates cobalt (§140).	Add dimethyl-glyoxime and warm. A scarlet precipitate shows nickel.
If sufficient nickel be present to obscure the blue bead, add to the solution of the sulphides (§133, 7) an excess of **nitroso-β-naphthol** in acetic acid solution (§132, 6*b*); filter, wash, and test the brick-red precipitate with the borax bead.	Or: Add excess of hot **KOH** and **Br**, boil, filter, wash (until filtrate gives no precipitate with $AgNO_3$), add solution of hot **KI** and test the filtrate with CS_2. If free iodine appears, nickel is present (§133, 6*f*).
The filtrate may be tested for nickel.	
Study §132, 6*c*, §135, §138, §139, §140, §141, §144, §135 and *ff*.	Study the text at §133, 6*a*, *b*, *e* and *f*; §132, 6*b* and *c*; §136, §138, §139, §140, §141, §144, §145 and *ff*.

Solution: $MnCl_2$, $ZnCl_2$(H_2S,HCl).

(traces of $CoCl_2$ and $NiCl_2$.)

Boil the solution thoroughly to remove the H_2S, cool, and add a decided excess of potassium or sodium hydroxide and bromine water and heat (§135, 6*a*). Filter and wash.

Precipitate:	**Solution:**
MnO_2 (traces of $Co(OH)_3$ and $Ni(OH)_3$.	K_2ZnO_2
Dissolve in HNO_3 + a small amount of H_2O_2 and boil. (If **Co** and **Ni** were present precipitate the manganese from this solution by $NH_4OH + H_2O_2$ and boiling. Filter, wash and redissolve in $HNO_3 + H_2O_2$ and boil.) Boil with HNO_3 and Pb_3O_4 or PbO_2. Manganese will give the reddish purple color of $HMnO_4$ (§134, 6*c*). Manganese may also be tested for, by pouring diamine over the MnO_2 if **Co** and **Ni** are absent, or if they are present, by pouring it over the precipitate of $Mn(OH)_3$ obtained by precipitating with $NH_4OH + H_2O_2$. Manganese gives a reddish purple precipitate.	Test for zinc by adding H_2S. A white precipitate (**ZnS**) indicates zinc.
Dark-colored original solutions indicating an alkali salt of manganese should be reduced by warming with **HCl** before proceeding with the analysis (§134, 5*c* and 6*f*).	Study the text at §135, 6*a* and *e*, §136, §138, §139, §142, §143, §144, §145 and *ff*.
Confirm by study of the text §134, 7, §136, §138, §139, §142, §143, §144, §145 and *ff*.	

* Small portions of cobalt and nickel sulphides may be dissolved by the cold dilute **HCl**, and will be precipitated with the $Mn(OH)_2$.

Directions for the Analysis of the Metals of the Fourth Group.

§138. Manipulation.—Into the warm strongly ammoniacal filtrate from the third group (§128), H_2S gas is passed until complete precipitation is obtained:

$$MnCl_2.2NH_4Cl + 2NH_4OH + H_2S = MnS + 4NH_4Cl + 2H_2O$$
$$(NH_4)_2ZnO_2 + 2H_2S = ZnS + (NH_4)_2S + 2H_2O$$

The solution is warmed until the precipitate subsides, allowed to stand for a few minutes, and is then filtered and the precipitate washed with hot water containing about one per cent of NH_4Cl (§139, *2*). The filtrate should be again tested with H_2S and if complete precipitation has been obtained it is set aside to be tested for the metals of the succeeding groups (§191). The well washed precipitate of the sulphides of **Co**, **Ni**, **Mn**, and **Zn** is digested on the filter or in a test-tube with **cold dilute HCl** (one part of reagent **HCl** to four of water): $MnS + 2HCl = MnCl_2 + H_2S$. The black precipitate remaining undissolved contains the sulphides of **Co** and **Ni**, the filtrate contains **Mn** and **Zn** as chlorides with an excess of **HCl** and the H_2S which has not escaped as the gas.

§139. *Notes.*—(*1*) Instead of passing the H_2S into the ammoniacal solution, a freshly prepared solution of ammonium sulphide may be used. The yellow ammonium sulphide, $(NH_4)_2S_x$, should not be employed to precipitate the metals of the fourth group, as nickel sulphide is quite appreciably soluble in that reagent (§133, 6*e*).

(*2*) The sulphides of the fourth group, especially **MnS** and **ZnS**, should not be washed with pure water, as they may be changed to the colloidal sulphides, soluble in water. The presence of a small amount of NH_4Cl prevents this, and does not in any way interfere with the analysis of the succeeding groups.

(*3*) If the precipitates are to be treated on the filter with the dilute **HCl**, the acid solution should be poured on the precipitate three or four times. For digestion in a test tube, the point of the filter is pierced and the precipitate washed into the test tube with as little water as possible.

(*4*) The sulphides of **Co** and **Ni** are not entirely insoluble in the cold dilute **HCl**, and traces of them may usually be detected in the precipitate for **Mn** (§137, footnote).

(*5*) Dilute acetic acid readily dissolves **MnS** but scarcely attacks **ZnS** (§135, 6*c*). If desired, dilute acetic may be used, first removing the **Mn** and then adding dilute **HCl** to dissolve the **Zn**.

(*6*) If large amounts of iron are present, a portion of the **Mn** will always appear in the third group (§134, 6*a*), and is detected by the green color of the fused mass when testing for **Cr**: $3Mn(OH)_2 + 4KNO_3 + Na_2CO_3 = 2K_2MnO_4 + Na_2MnO_4 + 4NO + CO_2 + 3H_2O$. Too much HNO_3 in the oxidation of the iron favors this precipitation of **Mn** with Fe''' due to the oxidation of the **Mn** to the triad or tetrad combination.

(*7*) Small amounts of the Fifth Group elements are carried down with the ammonium sulphide precipitate. As much as 5 mg. of barium may be present in this precipitate (Curtman & Frankel, *J. Am. Soc.*, **33**, 724, 1911).

§140. Manipulation.—The black precipitate of cobalt and nickel sulphides should first be tested with the borax bead (§141, *3*) for the blue bead of cobalt (delicate and characteristic but obscured by the presence of an excess of nickel (§132, 7)). The sulphides are then dissolved in hot **HCl**, using a few drops of HNO_3 (§141, *1*), and boiled to expel excess of HNO_3: $6CoS + 12HCl + 4HNO_3 = 6CoCl_2 + 3S_2 + 4NO + 8H_2O$. Divide the solution into three portions: To one portion of the solution

add an excess (§142, 2) of **nitroso-β-Naphthol**, filter, and wash with hot water and then with hot **HCl** (§132, 6*b*). Test the red precipitate with the borax bead for cobalt. Render the filtrate ammoniacal, filter again and test this last filtrate with H_2S for the black precipitate of **NiS** (§133, 6*b* and *e*). To another portion of the solution add $NaHCO_3$ in excess, then add H_2O_2, warm and filter, a *green* color to the filtrate indicates cobalt (§132, 10). The third portion of the solution is boiled with an excess of **NaOH**, bromine water (10, §§132 and 133) is added and the solution is again boiled. The black precipitate of the higher hydroxides (§141, 4) of **Co** and **Ni** is thoroughly washed with hot water and then treated on the filter with hot solution of **KI** (§133, 6*f*), catching this last filtrate in a test-tube containing CS_2 (§141, 6). Free iodine is evidence of the presence of nickel.

§141. *Notes.*—(1) HNO_3 interferes with the nitroso-β-naphthol reaction that follows the solution of the sulphides of **Co** and **Ni**, hence an excess is to be avoided. A crystal of $KClO_3$ may be used instead of HNO_3.

(2) If an insufficient amount of nitroso-β-naphthol has been used a portion of the cobalt may be in the filtrate and will give the black precipitate for nickel. The filtrate must be tested with the reagent to insure complete removal of the cobalt.

(3) Test with the borax bead as follows: Make a small loop on the end of a platinum wire, dip this loop when hot into powdered borax, and heat the adhering mass in the flame until a uniform transparent glassy bead is obtained. Repeat until a bead the size of a kernel of wheat has been made. Bring this hot bead into contact with the precipitate or solution to be tested and fuse again in the burner flame. Allow the bead to cool and notice the appearance. A deep blue indicates cobalt, obscured, however, by a large excess of nickel.

(4) The nickel and cobalt may also be oxidized for the **KI** test as follows: Add five or ten drops of bromine to the solution to be tested in a beaker, warm on a water bath under the hood until the bromine is nearly all expelled, then add rapidly an excess of a hot saturated solution of Na_2CO_3. The black precipitate so obtained will filter rapidly.

(5) The test for nickel by adding **KI** to the mixed higher oxides of cobalt and nickel is characteristic of nickel and is also a very delicate test. Fully nine-tenths of the cobalt salts sold for chemically pure, show the presence of nickel by this test.

(6) In the reaction of nickelic hydroxide with potassium iodide some potassium iodate is formed and a greater amount of free iodine will be obtained if a drop of hydrochloric acid be added to the filtrate: $KIO_3 + 5KI + 6HCl = 3I_2 + 6KCl + 3H_2O$

(7) If the sulphides of **Ni** and **Co** be digested with yellow ammonium sulphide, a portion of the **NiS** will be dissolved (§133, 6*c*) and may be reprecipitated as a gray precipitate (black with free sulphur) upon acidulating the filtrate with acetic acid. It is not a delicate test.

§142. **Manipulation.**—The solution of the sulphides of manganese and zinc in cold dilute hydrochloric acid is **boiled thoroughly** to insure the removal of the *hydrosulphuric acid* (§143, 1), cooled (§135, 6*a*), and then treated with an excess of sodium hydroxide. The zinc forms the soluble zincate, Na_2ZnO_2, while the manganese is precipitated as the hydroxide, white, rapidly turning brown by oxidation:

$$MnCl_2 + 2NaOH = Mn(OH)_2 + 2KCl$$
$$ZnCl_2 + 4NaOH = Na_2ZnO_2 + 2NaCl + 2H_2O$$

Filter and test the filtrate with H_2S, a white or grayish-white precipitate indicates zinc (**characteristic**). Dissolve the well washed precipitate of $Mn(OH)_2$ in nitric acid and boil with an excess of lead peroxide, adding more nitric acid. A violet color to the nitric acid solution indicates the presence of manganese (very **delicate** and **characteristic**):

$$2Mn(OH)_2 + 5PbO_2 + 10HNO_3 = 2HMnO_4 + 5Pb(NO_3)_2 + 6H_2O$$

§143. *Notes.—1.* If the H_2S is not completely removed the **Zn** will be precipitated as the sulphide upon adding the **NaOH**, and will not be separated from the manganese: $ZnCl_2 + H_2S + 2NaOH = ZnS + 2NaCl + 2H_2O$.

2. Frequently the precipitate of zinc sulphide is dark gray or almost black. This is usually due to the presence of traces of other sulphides. If iron has not been all removed, through failure to oxidize completely with the nitric acid, it may appear as a precipitate with the manganese, and also as a black precipitate with the zinc sulphide.

3. Small amounts of **Co** and **Ni** are frequently dissolved by the cold dilute **HCl** and will appear with the precipitate of $Mn(OH)_2$. They do not interfere with the final test for manganese.

4. The precipitate of $Mn(OH)_2$ must be washed to remove all the chloride, as the manganese will not be oxidized to permanganic acid until the chloride is completely oxidized to chlorine.

5. Instead of PbO_2, red lead, Pb_3O_4, is frequently employed with the nitric acid to oxidize the manganese to permanganic acid:

$$2Mn(OH)_2 + 5Pb_3O_4 + 30HNO_3 = 2HMnO_4 + 15Pb(NO_3)_2 + 16H_2O$$

6. It is very difficult to procure PbO_2 or Pb_3O_4 which does not contain traces of manganese. The student should always boil the lead oxides with nitric acid, and if a violet-colored solution is formed, this should be decanted and the operation repeated until the solution is perfectly colorless after the black precipitate of PbO_2 has subsided. Then the unknown solution in HNO_3 may be added and the boiling repeated to test for the manganese.

7. The student is not advised to apply the permanganate test to the original substances. All reducing agents interfere, and MnO_2 frequently fails to give permanganic acid when boiled with PbO_2 and HNO_3 until after reduction (§134, 6*c*).

Analysis of Iron and Zinc Groups after Precipitation by Ammonium Sulphide.

§144. It is preferred by some to precipitate the metals of the third and fourth groups together, by means of **ammonium sulphide**; using **ammonium chloride** to prevent the precipitation of magnesium (§189, 5*b* and 6*a*), and to insure the complete precipitation of the aluminum as the hydroxide §124, 6*a*). In the manipulation for this method of separation, the H_2S is not removed from the second group-filtrate, nor is nitric acid used to oxidize any iron that may be present. To the *second group filtrate* (§80), warmed, an excess of NH_4Cl is added (§189, 5*c*), then NH_4OH till strongly alkaline, and, paying no attention to any precipitate that may be formed (6*a*, §§124, 125 and 126), normal **ammonium sulphide** is added (or what is equivalent H_2S is passed into the alkaline mixture). **Aluminum** and **chromium** are precipitated as the *hydroxides*, the remaining metals as the *sulphides*. The following table illustrates a plan of separation of the **ammonium sulphide** precipitates of the **third** and **fourth group** metals, phosphates being absent:

Dissolve the well-washed precipitate, on the filter, by **cold dilute hydrochloric acid.** Filter and wash.

Residue:

CoS, NiS (black).

Dissolve in nitro-hydrochloric acid and separate and identify as directed in §137 and *ff*.

Solution: $FeCl_2$, $AlCl_3$, $CrCl_3$, $MnCl_2$, $ZnCl_2$, ($CoCl_2$, $NiCl_2$).*

Boil the solution to expel the H_2S and add a few drops of HNO_3 and again boil to oxidize the iron; then add a large *excess* of **NaOH** and *boil*. Filter and wash.

Residue:

$Cr(OH)_3$, $Fe(OH)_3$, $Mn(OH)_2$, $[Co(OH)_2, Ni(OH)_2]$.

Dissolve the residue in **HCl**, add NH_4Cl, and then an excess of NH_4OH. Filter.

Residue:

$Fe(OH)_3$, $Cr(OH)_3$.

Dissolve in **HCl** and then add an excess of cold **NaOH** (§131, *1*). Filter.

Residue:

$Fe(OH)_3$.

Dissolve in **HCl** and add **KCNS**.

§126, 6*a*, §127 and *ff*.

Solution:

Na_2CrO_2.

Oxidize the Cr''' to Cr^{VI} with chlorine water, add acetic acid and test with $BaCl_2$ (§186, 6*h*).

Solution:

$MnCl_2.2NH_4Cl$.

(Co and Ni traces.)*

Precipitate with H_2S. Filter and wash; boil the precipitate with HNO_3 and PbO_2.

§134, 6*c*, §137 and *ff*.

Solution: $NaAlO_2$, Na_2ZnO_2.

Acidify with **HCl** and add an excess of NH_4OH.

Precipitate:

$Al(OH)_3$.

Confirm by dissolving in **KOH** and reprecipitating with NH_4Cl.

§124, 6*a*, §127 and *ff*.

Solution:

$(NH_4)_2ZnO_2$.

Add H_2S. White precipitate, **ZnS**.

§135, 6*e*, §137 and *ff*.

* The cold dilute **HCl** frequently dissolves traces of cobalt and nickel sulphides (§137, footnote).

§145. The presence of **phosphates** greatly complicates the work of the analysis of the metals of the third, fourth, and fifth groups. The phosphates of the alkali metals are soluble, those of the other metals insoluble in water. As the solutions for precipitation of first and second group metals are acid; phosphates remain in solution and do not in any way interfere with the analysis for the metals of those groups; *i. e.*, silver phosphate in nitric acid solution is readily transposed by **HCl**; copper phosphate in acid solution is readily transposed by $\mathbf{H_2S}$; etc.

§146. When the filtrate from the second group is rendered strongly ammoniacal (§128) the phosphates of all the metals present, except those of the alkalis, are precipitated. Phosphates of cobalt, nickel and zinc are redissolved by an excess of ammonium hydroxide. Freshly precipitated ferric phosphate is transposed by the alkali hydroxides (incompletely in the cold). The phosphates of **Al**, **Cr**, and **Zn** are soluble in the fixed alkalis, the solution of chromium phosphate is decomposed by boiling, precipitating $\mathbf{Cr(OH)_3}$ and leaving the alkali phosphates in solution.

§147. In **analysis** a portion of the filtrate from the second group (after the removal of the $\mathbf{H_2S}$) (§128) should be tested for phosphoric acid with ammonium molybdate (§75, 6*d*). If phosphates are present the usual methods of analysis for third, fourth, and fifth groups must be modified. Several methods have been recommended:

§148. **First.**—To the filtrate from the second group, $\mathbf{H_2S}$, being removed (§128), an excess of the reagent **ammonium molybdate** is added, the mixture set aside in a warm place for several hours, until the yellow ammonium phospho-molybdate has completely formed and settled (§75, 6*d*). Filter and evaporate nearly to dryness to remove the nitric acid. Take up with water and a little hydrochloric acid if necessary to obtain a clear solution, and remove the excess of molybdenum with $\mathbf{H_2S}$ (§75, 6*e*). From this point proceed by the usual methods of analysis (§§127, 128 and *ff.*).

§149. **Second.—Precipitation of the phosphate as ferric phosphate in acetic acid solution.** This method of separation rests upon the fact that the *phosphates* of the fourth group and of the *alkaline earths* are soluble, and the phosphates of **Al**, $\mathbf{Cr'''}$ and $\mathbf{Fe'''}$, insoluble in *acetic acid.*

To the filtrate from the second group, freed from $\mathbf{H_2S}$ by boiling (128), and nearly neutralized with $\mathbf{Na_2CO_3}$, an excess of $\mathbf{NaC_2H_3O_2}$ is added and then $\mathbf{FeCl_3}$ solution, drop by drop, as long as a precipitate is formed. Care must be taken to avoid an excess of $\mathbf{FeCl_3}$, as the ferric phosphate is soluble in a solution of ferric acetate. As soon as the phosphate is all precipitated the blood-red ferric acetate is formed at once, indicating the presence of a sufficient amount of $\mathbf{FeCl_3}$. The mixture should be boiled

to precipitate the ferric acetate as basic ferric acetate (§126, 6*b*) and at once filtered.

Upon the addition of the sodium acetate the aluminum and chromium are precipitated as phosphates, provided there be sufficient phosphate present to combine with them; if not the whole of the phosphate will be precipitated and the first drop of $FeCl_3$ will give a red solution showing the addition of that reagent to be unnecessary.

By the above method of manipulation any iron present in the original solution is in the *ferrous* condition and does not react to precipitate the phosphate, as *ferrous phosphate* is *soluble* in *acetic acid*. If the iron has been previously oxidized with nitric acid it will react with the phosphate upon the addition of the sodium acetate; but if there be more iron present than necessary to combine with the phosphate, the red ferric acetate solution will be formed with the excess of the iron and render the precipitation of the phosphate incomplete. In this case the previous oxidation of the iron is detrimental.

If alkaline earth salts are present in quantity more than sufficient to combine with the phosphoric acid radical, not all of these metals will be precipitated with the third group metals upon the addition of ammonium hydroxide. The table (§152) illustrates the separation of the metals in presence of the phosphates by the use of $FeCl_3$ in acetic acid solution.

§150. **Third.**—A method of separation of the third group metals with phosphates from the remaining metals is based upon the action of freshly precipitated **barium carbonate.** Solutions of Al, Cr''', and Fe''' are precipitated as the hydroxides by digestion in the cold with freshly precipitated $BaCO_3$ (6*a*, §§124, 125 and 126): $2AlCl_3 + 3BaCO_3 + 3H_2O = 2Al(OH)_3 + 3BaCl_2 + 3CO_2$. Solutions of the chlorides or nitrates of the fourth group and of the alkaline earths are not transposed by cold digestion with $BaCO_3$. *Sulphates* of the fourth group are transposed by freshly precipitated $BaCO_3$ in the cold: $CoSO_4 + BaCO_3 = BaSO_4 + CoCO_3$, etc.; and must not be present in this method of separation (§126, 6*a*).

If an excess of ferric chloride be present the phosphates will all be precipitated as ferric phosphate and the Al, Cr''' and excess of Fe''' as the hydroxides upon the digestion with $BaCO_3$. The table (§153) gives an illustration of the use of the $BaCO_3$ in effecting the separation.

It should be observed that presence or absence of $FeCl_3$ or of $BaCO_3$ in the sample must be fully determined before their addition as reagents.

§151. **Oxalates** do not interfere with the usual course of analysis of the first two groups of metals; with the other metals oxalates interfere very much the same as phosphates. They, however, with other interfering

organic matter, can readily be removed by ignition. If the presence of an oxalate has been established (§§**188**, 6*b* and **227**, 8), the second group filtrate should be evaporated to dryness, moistened with concentrated HNO_3 and gently ignited. The residue, dissolved in **HCl**, is then ready for the usual process of analysis. For the analysis in presence of silicates and borates the student is referred to the text under those elements (§§**249**, 8 and **221**, 8).

§152. Separation of Iron, Zinc, and Calcium Group Metals and Phosphoric Acid from each other, by Use of Alkali Acetate and Ferric Chloride (§149).

To the clear filtrate from the Second Group, freed from H_2S by boiling, add a few drops of **nitric acid**, and boil an instant; then at once precipitate by **ammonium chloride** and excess of **ammonium hydroxide** (§127). Filter and precipitate by **ammonium sulphide** (§137). Filter and reserve this filtrate for the Fifth * and Sixth Groups (§190 §211 and *ff.*) Wash both precipitates separately, and digest them together, in an evaporating dish, with ammonium sulphide. Filter and wash.† (For rare metals, see §154 and *ff.*)

Residue: $AlPO_4$, $Al(OH)_3$, $CrPO_4$, $Cr(OH)_3$; FeS, CoS, NiS, MnS, ZnS; Ba, Sr, Ca and Mg Phosphates.

Dissolve the residue in hot dilute **hydrochloric acid**, with the addition of a minute fragment of **potassium chlorate.** Boil to expel free chlorine, and filter out any free sulphur. Render the solution nearly neutral with **sodium carbonate,** and add a solution of **sodium acetate** strongly acidified with **acetic acid,** as long as a precipitate results. Digest with gentle heat, and filter while hot.

Precipitate: $AlPO_4$, $CrPO_4$, $FePO_4$.

Boil the precipitate for some time with a fixed alkali hydroxide (§146).

Residue: $Cr(OH)_3$, $Fe(OH)_3$.

Test as directed in §127.

Solution:

$KAlO_2$, or $NaAlO_2$ with an alkali phosphate.

Acidulate with HNO_3 and add an excess of NH_4OH.

Precipitate: $AlPO_4$, insoluble in acetic acid.

Or, separate the **Al** and PO_4 as directed in §124, 6*d* and 7.

Confirm the presence of a phosphate by $(NH_4)_2MoO_4$ in the solution acidulated with HNO_3, and also test for a phosphate in the filtrate from the NH_4OH precipitate of $AlPO_4$.

Solution: ($AlCl_3$, $CrCl_3$, $FeCl_3$ or H_3PO_4); $CoCl_2$, $NiCl_2$, $MnCl_2$, $ZnCl_2$; $BaCl_2$, $SrCl_2$, $MgCl_2$, $CaCl_2$.

Test a small portion for phosphoric acid with molybdate solution. If phosphoric acid is absent neutralize the remainder of the solution with ammonia, warm and add any precipitate of $Fe(OH_3)$, $Al(OH)_3$ and $Cr(OH)_3$ to the precipitate of iron, aluminum, and chromium phosphates. If phosphoric acid is present add **Ferric Chloride** drop by drop (§149), as long as a precipitate results, and until the liquid turns red, and digest for some time at gentle heat. Filter and reject the precipitate, $FePO_4$. To the filtrate add **ammonium hydroxide,** warm and reject the precipitate of $Fe(OH)_3$.

Precipitate:

$Al(OH)_3$, $Cr(OH)_3$, [$Fe(OH)_3$].

Follow §127.

Filtrate:

Fourth and Fifth Groups.

Follow as for analysis in absence of phosphates (§137 and §190).

* Any alkaline earths found in this filtrate are in excess of the amount necessary to combine with the phosphoric acid radical.

† Phosphoric acid found here, shows that some phosphates, (Fe''' or **Mn**) had been precipitated by ammonium hydroxide and then decomposed by ammonium sulphide.

§153. Separation of Iron, Zinc, and Calcium Group Metals and Phosphoric Acid from each other, by means of Ferric Chloride and Barium Carbonate (§150).

To the filtrate from the Second Group (§80), add **ammonium chloride** and **ammonium hydroxide** to alkaline reaction, then **ammonium sulphide** (§144) to complete the precipitation. Reserve the filtrate for the Fifth Group (§190).

Precipitate: FeS, MnS, CoS, NiS, ZnS, S; $Al(OH)_3$, $Cr(OH)_3$; phosphates of **Al**, **Cr‴** and of **Ba**, **Sr**, **Ca** and **Mg**.

Treat the well-washed precipitate with cold dilute hydrochloric acid. If a black residue remains, test it for **Co** and **Ni**, as directed in the table at §137. Also, this residue may be tested for **Si** (§249, 8). The filtered solution is *boiled* to expel H_2S, and a smaller portion reserved (§150).

Portion 1.

Add a few drops of **nitric acid** and boil.

Solution: $AlCl_3$, $CrCl_3$, $FeCl_3$, ($CoCl_2$, $NiCl_2$), $MnCl_2$, $ZnCl_2$, $BaCl_2$, $SrCl_2$, $CaCl_2$, $MgCl_2$, H_3PO_4, (H_2SiO_3).

(1) Test a small portion for iron (§150), by thiocyanate. If iron is found, test the original solution by ferricyanide and thiocyanate as directed in §126, 6*b* and §130.

(2) To the remainder, add **Ferric Chloride** till a drop is precipitated yellow by ammonium hydroxide (showing that the PO_4 is all precipitated), concentrate to a small bulk, add water, nearly neutralize by K_2CO_3, and add an excess of freshly precipitated **Barium Carbonate**. Let the mixture stand twelve hours and filter (§126, 6*a*).

Portion 2 (smaller).

Add sulphuric acid and filter (§177). Fuse the precipitate in a crucible with a mixture of molecular proportions of Na_2CO_3 and K_2CO_3 (§205, 7). Allow to cool; digest with water, filter, wash and dissolve the precipitate of **Ba**, **Sr** and **Ca** carbonates in acetic acid, and analyze as in absence of phosphates, especially for barium (§190).

Precipitate:

$Al(OH)_3$, $Cr(OH)_3$, [$FePO_4$, $Fe(OH)_3$, $BaCO_3$].

Boil the precipitate for some time with sodium or potassium hydroxide.

Residue:

$Cr(OH)_3$, [$Fe(OH)_3$.$BaCO_3$].

Test for **chromium** as directed (§127).

Solution:

$KAlO_2$ and alkali phosphate. Acidify with **HNO_3** and add an excess of **NH_4OH**.

Precipitate: $AlPO_4$, insoluble in acetic acid.

Test for phosphate in the **HNO_3** solution with **$(NH_4)_2MoO_4$** (§75, 6*d*).

Study §124, 6*d* and 7.

Solution:

$MnCl_2$, $ZnCl_2$, $SrCl_2$, $CaCl_2$, $MgCl_2$ [$BaCl_2$, CO_2].

Add **HCl** and boil to expel **CO_2**. Add **NH_4OH** to alkaline reaction, then ammonium sulphide (or **H_2S**), and warm and filter.

Precipitate: MnS, ZnS.

Dissolve by cold dilute **HCl** * and follow as in analysis in absence of phosphates (§137).

Solution:

$CaCl_2$, $SrCl_2$, $MgCl_2$, [$BaCl_2$].

Remove the **Ba**, **Sr** and **Ca** as directed in Portion 2, above, then add ammonium oxalate and hydroxide, filter and test for **Mg** in the filtrate by **Na_2HPO_4** (§189, 6*d*).

Or, analyze as directed in absence of phosphates (§190).

* Traces of **Co** and **Ni** as sulphides may remain, also a black residue. Test as directed in §137.

The Rarer Metals of the Iron and Zinc Groups.

Cerium, Columbium (Niobium), *Didymium*, **Erbium, Gallium, Glucinum** (Beryllium), **Indium, Lanthanum, Neodymium, Praseodymium, Samarium, Scandium, Tantalum, Terbium, Thallium, Thorium, Titanium, Uranium, Vanadium, Ytterbium, Yttrium, Zirconium.**

§154. Cerium. Ce = 140.25. Valence three and four.

Specific gravity, 6.628. *Melting point*, 640° (*Cir. B. of S.*, 1915). Cerium is a comparatively rare metal, never found native; it is found in many minerals in Sweden, especially in cerite, which is chiefly a silicate of **Ce**, **La**, **Ne**, **Pr**, **Al** and **Fe**; also found in a brick-making clay near Frankfurt, Germany (Strohecker, *J. pr.*, 1886, (2), **33**, 133 and 260). It was first described in 1803 by Klaproth, but in 1839 Mosander showed the supposedly pure cerium oxide to consist of oxides of at least three metals: **Ce**, **La**, **D** (**Ne** and **Pr**) (*Pogg.*, 1842, **56**, 503). Commercial "cerium" consists of all of these metals in varying proportion and is known as mixed metal (misch metal). The metal is obtained from the chloride, $CeCl_3$, by electrolysis or by heating with sodium. It is a steel-gray, lustrous, malleable, ductile metal; fairly stable in air under ordinary conditions. When heated in air it burns with incandescence. The impure commercial cerium is alloyed with iron and other heavy metals and used in friction ignition devices. The iron alloy is known as auermetal. It burns in **Cl**, **Br** and in vapor of **I**, **S** and **P**. Soluble in acids. Two oxides are known, Ce_2O_3 and CeO_2, forming two classes of salts, cerous and ceric, the latter being less stable. Ignition in air or oxygen changes Ce_2O_3 to CeO_2. Ce_2O_3 is white or grayish-white, soluble in acids and formed by igniting $Ce_2(CO_3)_3$, $Ce_2(C_2O_4)_3$ or CeO_2 in an atmosphere of hydrogen. Cerous salts are white and form colorless solutions in water. Ceric oxide, CeO_2, is yellowish-white, orange-yellow when hot, soluble in acids with difficulty; the hydroxide dissolves readily. Ceric salts are yellow or red, forming yellow solutions. Ceric hydroxide, $Ce(OH)_4$, dissolves in **HCl** with evolution of *chlorine*, forming colorless cerous chloride. Sulphurous acid decolorizes solutions of ceric salts, forming cerous salts. **Fixed alkali hydroxides** and **ammonium sulphide** precipitate, from solutions of cerous salts, the white *cerous hydroxide*, turning yellow by absorption of oxygen, with formation of ceric hydroxide. The precipitate is insoluble in excess of the fixed alkalis (distinction from **Al** and **Gl**). The precipitation is hindered by the presence of tartaric acid (distinction from yttrium). **Ammonium hydroxide** precipitates a basic salt; if H_2O_2 is added before neutralizing a reddish brown precipitate is formed (*delicate* test for cerium). **Alkali carbonates** precipitate cerous carbonate, soluble in excess of the fixed alkali carbonates. **Oxalic acid** forms *cerous oxalate*, white, from moderately acid solutions, soluble in hot $(NH_4)_2C_2O_4$, but reprecipitated on dilution with cold water. The oxalate is less soluble in hot than in cold water. A concentrated solution of K_2SO_4 forms the *double sulphate*, $K_3Ce(SO_4)_3$, white, sparingly soluble in water, insoluble in K_2SO_4 solution (distinction from **Gl**). $Na_2S_2O_3$ does not precipitate cerium salts. $BaCO_3$ does not precipitate cerous salts in the cold, but precipitates them completely on boiling. *Ceric salts* are completely precipitated by $BaCO_3$ in the cold. **Alkali hypochlorites** precipitate cerous salts as the yellow ceric hydroxide. If cerous nitrate be boiled with PbO_2 and HNO_3, *ceric nitrate*, a deep yellow solution, is formed (*delicate* test for cerium). Cerium gives no absorption spectrum, but the spark spectrum shows several brilliant lines.

§155. Columbium (Niobium). Cb = 93.5. Valence five.

Columbium usually occurs with tantalum in such minerals as columbite and tantalite; it is also found in tantalum free minerals as euxenite, pyrochlor, etc. The metal is prepared by passing the penta-chloride mixed with hydrogen repeatedly through a hot tube. It is a steel-gray lustrous metal, *specific gravity*, 7.06 at 15.5° *Melting point*, ±1700 (*Cir. B. of S.*, 1915). By ignition in the

air it burns readily to the pentoxide. Not attacked by chlorine in the cold, but when warmed combines readily, forming **$CbCl_5$**. The metal is not soluble in hydrochloric, nitric or nitrohydrochloric acid, but is readily soluble in hot concentrated sulphuric acid, forming a colorless solution (Roscoe, *C. N.*, 1878, **37**, 25). It forms several oxides, **CbO**, **CbO_2** and **Cb_2O_5**. Columbic acid (anhydride) **Cb_2O_5**, is a white powder, yellow when hot (distinction from tantalum); it is obtained by ignition of the lower oxides, or by decomposition of solutions of the salts by water or alkalis and igniting. **CbO_2**, black, is prepared by strongly igniting **Cb_2O_5** in a current of hydrogen. **Cb_2O_5**, not too strongly ignited, is soluble in acids, from which solutions **NH_4OH** and **$(NH_4)_2S$** precipitate *columbic acid* containing some ammonia. By mixing **Cb_2O_5** with charcoal and heating in a current of chlorine, a mixture of **$CbOCl_3$** and **$CbCl_5$** is obtained. **$CbCl_5$** is a yellow crystalline solid (needles), melting at 194° and distilling at 240.5° (Deville and Troost, *C. r.*, 1867, **64**, 294). Upon treating the chloride with water, it is partially decomposed to columbic acid, a large portion remaining in solution and not precipitated by **H_2SO_4** (distinction from tantalum). **Cb_2O_5** not previously ignited dissolves in **HF**; which solution, when mixed with **KF**, the **HF** being in excess, gives a double fluoride, **$2KF.CbF_5$**; if the **HF** be not in excess, a double oxy-fluoride is obtained, **$2KF.CbOF_3$** (Kruess and Nilson, *B.*, 1887, **20**, 1676). The potassium columbium fluoride is much more soluble than either the corresponding titanium or tantalum compounds. Fusion of columbic acid with the alkalis gives the columbates, the *potassium salt* being quite soluble in water and in potassium hydroxide; the *s dium salt* is only soluble in water after removal of the excess of the sodium hydroxide. From a solution of potassium columbate, **sodium hydroxide** precipitates, almost completely, *sodium columbate*. **Carbon dioxide** precipitates *columbic acid* from solutions of columbates. Soluble salts of **Ba**, **Ca** and **Mg** form white bulky precipitates with a solution of potassium columbate. **$AgNO_3$** gives a yellowish-white precipitate, **$CuSO_4$** a green precipitate. **Cb_2O_5** in presence of **HCl** or **H_2SO_4**, gives a *blue* to *brown color* with **Sn** or **Zn**, due to partial reduction of the **Cb** (distinction from tantalum). Fused with sodium meta-phosphate, columbic acid gives in the inner flame a violet to blue bead; a red bead by addition of **$FeSO_4$**.

§156. Didymium = { **Neodymium.** **Nd** = 144.3. Valence three. / **Praseodymium.** **Pr** = 140.9. Valence three.

Specific gravity, 6.544. *Melting points*, Neodymium, 840?; praseodymium, 940? (*Cir. B. of S.*, 1915). Present in cerite in Sweden and in monazite sand from Brazil. Didymium was reported about 1840 by Mosander, having been separated from cerium and lanthanum. In 1885 Welsbach (*M.*, 1885, **6**, 477) separated didymium salts into two distinct salts, neodymium and praseodymium. By the absorption spectrum bands other chemists are of the opinion that the so-called didymium consists of a group of elements, nine or more (Kruess and Nilson, *B.*, 1887, **20**, 2166; Kruess, *A.*, 1892, **265**, 1). Concerning the separation of didymium compounds, see Dennis and Chamot (*J. Am. Soc.*, 1897, **19**, 799). By repeated fractionation of the nitrate (several thousand times) Welsbach obtained a pale green salt and a rose-colored salt, which gave different spectra, but which, united, gave the spectrum of didymium. Didymium oxide absorbs water to form the hydroxide, which absorbs **CO_2** from the air, but does not react alkaline to litmus. The salts are soluble in water to a reddsih solution. The saturated sulphate solution does not deposit crystals *until heated to boiling*; while *lanthanum sulphate precipitates* from the saturated solution at **30°**. **Fixed alkalis** precipitate the hydroxide: **NH_4OH**, a basic salt; insoluble in excess of the reagents. **Alkali carbonates** form a bulky precipitate, insoluble in excess of the reagent, **barium carbonate** precipitates slowly but completely. Precipitation by alkalis is prevented by tartaric acid. **Oxalic acid** precipitates didymium salts completely, soluble with difficulty in **HCl**. The double potassium sulphate forms much more slowly and less completely than with cerium. The salts give a distinct and *characteristic* absorption spectrum. Consult Jones, (*Am.*, 1898, **20**, 345), Schele (*Z. anorg.*, 1898, **17**, 319), Boudard (*C. r.*, 1898, **126**, 900), Demarcay (*C. r.*, 1898, **126**, 1039), and Brauner (*C. N.*, 1898, **77**, 161).

§157. Erbium. Er = 167.7. Valence three.

Erbium has been prepared in the form of a dark gray powder. *Specific gravity*, 4.77 at 15°. (Meyer, *Monatsch.*, **20**, 793, 1899). As oxide or earth it is described by Cleve (*C. r.*, 1880, **91**, 381) as that yttrium earth the most beautiful rose colored. It forms a *characteristic* absorption spectrum, and a spark spectrum with sharp lines in the orange and green. This earth has not been thoroughly studied and quite probably consists of the oxides of several metals (Boisbaudran, *C. r.*, 1886, **102**, 1003; Soret, *C. r.*, 1880, **91**, 378; Crookes, *C. N.*, 1886, **54**, 13). The oxide gives upon ignition an intense green light; it is not fusible or volatile.

§158. Gallium. Ga = 69.9. Valence three.

Specific gravity, the solid, at 23° to 24.5°, 5.935 to 5.956; the melted, at 24.7°, 6.069. *Melting point*, 30.15°; frequently may be cooled to 0° without again becoming solid. It is a grayish-white metal, crystallizing in octahedra or in broad plates. It is quite brittle and gives a bluish-gray mark on paper. It gives a very weak and fugitive flame spectrum; the spark spectrum shows two beautiful violet lines. When heated in the air or in oxygen it is but slightly oxidized; does not vaporize at a white heat; soluble in acids and alkalis; attacked by the halogens (with iodine only upon warming). In the Periodic System it is the Ekaaluminum of Mendelejeff, who described the general properties before the metal was discovered (*C. r.*, 1875, **81**, 969). It occurs in zinc blende (black) from Bensberg on the Rhine; in brown blende from the Pyrenees; and in some American zinc blendes (Cornwall, *Ch. Z.*, 1880, **4**, 443). It is prepared by electrolysis after previous purification of the ore by chemical methods. 4300 kilos of the Bensberg ore gave 55 kilos of pure gallium (Boisbaudran and Jungfleisch, *C. r.*, 1878, **86**, 475). The oxide, Ga_2O_3, is a white powder obtained by igniting the nitrate. After strong ignition it is insoluble in acids or alkalis. It is easily attacked on fusion with **KOH** or $KHSO_4$. The **alkalis** and the **alkali carbonates** precipitate the salts as the hydroxide, perceptibly soluble in fixed alkali carbonates, more easily in ammonium hydroxide and in ammonium carbonate, and very readily in the fixed alkalis. Tartrates hinder the precipitation of the hydroxide. The salts of gallium are colorless and for the most part soluble in water. The neutral solutions upon warming precipitate a basic salt, dissolving again upon cooling. Excess of zinc forms a basic zinc salt which precipitates the gallium as oxide or basic salt. $BaCO_3$ precipitates gallium salts in the cold. $K_4Fe(CN)_6$ gives a precipitate, insoluble in **HCl**, noticeable in very dilute solutions (1-175,000). H_2S does not precipitate gallium salts from solutions acid with mineral acids; from the acetate or in presence of ammonium acetate the *white sulphide*, Ga_2S_3, is precipitated; $(NH_4)_2S$ precipitates the sulphide. Gallium chloride, $GaCl_3$, is a colorless salt, melting at 75° and volatilizing at 215° to 220°. The vapor density indicates the molecule to be Ga_2Cl_6, which decomposes to $GaCl_3$ at about 400° (Friedel and Kraft, *C. r.*, 1888, **107**, 306). Upon evaporating a solution of the chloride on a water bath the salt is perceptibly volatilized, not so if H_2SO_4 be present. Gallium sulphate forms with ammonium sulphate an alum. For separation from other metals, see Boisbaudran, *C. r.*, 1882, **95**, 410, 503, 1192, 1332.

§159. Glucinum (Beryllium). Gl = 9.1. Valence two.

Specific gravity, 1.85 (Humpidge, *Proc. Roy. Soc.*, 1871, 39, 1). *Melting point*, 1350° ? (*Cir. B. of S.*, 1915). It is a white malleable metal, obtainable in hexagonal crystals (Nilson and Pettersson, *B.*, 1878, **11**, 381 and 906). It was first discovered in 1797 by Vauquelin from beryl. The powdered metal takes fire when heated in air, burning with great brilliancy. It dissolves readily in dilute acids and also in alkalis with evolution of hydrogen. It does not decompose steam even at a red heat. It is a strongly positive element, in general properties between aluminum and the alkaline earths; as lithium is between the alka-

line earths and the alkali metals. It should be classed with the alkaline earths. It is found in chrysoberyl, $Gl(AlO_2)_2$, in phenakite, Gl_2SiO_4, and in some other silicates. It is prepared by heating the chloride, $GlCl_2$, with **Na** in a closed iron crucible (Nilson and Pettersson, *l. c.*); or by heating the oxide, **GlO**, with **Mg** (Winkler, *B.*, 1890, **23**, 120). The oxide, **GlO**, is obtained by igniting the hydroxide. It is a white infusible powder, soluble in acids and in fixed alkalis. The hydroxide is prepared by precipitating the salts with NH_4OH, soluble in the *fixed alkalis* and in *ammonium carbonate*, concentrated; precipitated on dilution and boiling (distinction and separation from **Al**). The metal is soluble in acids except that when in the compact form it is scarcely attacked by HNO_3. The hydroxide is soluble on continued boiling with NH_4Cl, forming $GlCl_2$. The more common salts of glucinum are soluble in water to a solution having a sweetish taste. The carbonate and phosphate are insoluble, the oxalate and sulphate soluble, the existence of a sulphide is doubtful. Solutions of glucinum salts are precipitated by the **alkalis,** the precipitate being soluble in excess of the fixed alkalis. The **alkali carbonates** precipitate the carbonate, soluble in concentrated ammonium carbonate, reprecipitated on diluting, boiling and adding an excess of NH_4OH (Joy, *Am. S.*, 1863, (2), **36**, 83). The salts are not precipitated by H_2S, but are precipitated by $(NH_4)_2S$ as the hydroxide. $BaCO_3$ does not precipitate **Gl** salts in the cold, but precipitates them upon boiling. $GlCl_2$ melts at about 600° and sublimes at a white heat, forming white needles. The oxide has not been melted or sublimed. **Gl** usually occurs as a silicate with aluminum. The mass is fused with alkali carbonate, acidified with **HCl** and the **Al** and **Gl** chlorides filtered from the SiO_2. An excess of ammonium carbonate precipitates both metals, but redissolves the **Gl**. After repeating this separation several times pure glucinum hydroxide, $Gl(OH)_2$, is obtained upon boiling off the ammonia. The hydroxide thus obtained is ignited and weighed as the oxide.

§160. Indium. In = 114.8. Valence three.

Specific gravity, 7.11 to 7.28 at 20.4°. *Melting point*, 155° (*Cir. B. of S.*, 1915). Indium was discovered in Freiberg zinc blende by Reich and Richter (*J. pr.*, 1863, **89**, 441; **90**, 175; 1864, **93**, 480), by use of the spectroscope. It is found chiefly as sulphide, never native, in the Freiberg blende to the extent of about 0.1 per cent. It is found in a few other places, but in much smaller amounts (Boettger. *J. pr.*, 1866, **98**, 26). In the preparation of indium the Freiberg zinc is dissolved in **HCl** or H_2SO_4, leaving an excess of the zinc. When no more hydrogen is evolved, the mass is digested for a day or more with the excess of **Zn**, whereby the indium is obtained as a precipitate with **Pb**, **Cu**, **Cd**, **Sn**, **As**, **Fe** and **Zn**. This precipitate is dissolved in nitric acid and evaporated with sulphuric acid; then taken up with water, separating from lead. The solution is precipitated with NH_4OH, which precipitates the **In** and **Fe**; this precipitate is dissolved in **HCl** and boiled for some time with $NaHSO_3$. The indium sulphite is obtained as a fine crystalline powder, which is treated with HNO_3 and H_2SO_4, forming indium sulphate, from which the metal is precipitated by zinc (Bayer, *A.*, 1871, **158**, 372; Boettger, *J. pr.*, 1869, **107**, 39; Winkler, *J. pr.*, 1867, **102**, 276). Indium is a grayish-white metal, very soft, makes a good mark on paper, is ductile, easily fusible, less volatile than **Zn** or **Cd**. It is less electro-positive than **Zn** or **Cd** and hence it is precipitated from its solutions by both these elements. In the air or in water it is rather more stable than zinc. Heated in the air it burns with a violet flame and brown smoke, forming the oxide, In_2O_3. Indium does not decompose water at 100°. At a red heat it combines with sulphur and the halogens. By ignition with charcoal or in a current of hydrogen it is reduced to the metal from its compounds. It is soluble in **HCl** and H_2SO_4, evolving **H**; in HNO_3, evolving **NO**. In the reactions of its salts indium deports itself quite similar to Fe''' and **Al**. Its most *characteristic* property is its spectrum; two lines, an indium α, intense blue, and an indium β, less intense violet (Schroetter, *J. pr.*, 1865, **95**, 441). In_2O_3 is brown when hot, light yellow when cold, slowly soluble in cold acids, rapidly when heated. Indium salts are precipitated by the **alkalis** as $In(OH)_3$, soluble in excess of the fixed alkalis,

reprecipitated by boiling or treating with NH_4Cl. Tartrates prevent the precipitation by alkalis. **Alkali carbonates** precipitate the indium carbonate, soluble in ammonium carbonate, but reprecipitated on boiling. $BaCO_3$ precipitates the indium completely as a basi salt (separation from **Co**, **Ni**, **Mn**, **Zn** and **Fe**''). Phosphates form white precipitates from neutral solutions. H_2S precipitates from neutral solutions, or solutions acid with acetic acid, yellow indium sulphide. In alkaline solutions H_2S, or in neutral solutions $(NH_4)_2S$, forms a white precipitate containing In_2S_3. Yellow In_2S_3 boiled with $(NH_4)_2S_x$ becomes white and is partly dissolved. Upon cooling the solution a bulky white precipitate separates out. $K_4Fe(CN)_6$ gives a white precipitate; K_2CrO_4 gives a yellow precipitate; $K_2Cr_2O_7$, $K_3Fe(CN)_6$ and **KCNS** do not form precipitates.

§161. Lanthanum. La = 139.0. Valence three.

Specific gravity, 6.163. *Melting point*, 810° ? (*Cir. B. of S.*, 1915). In general appearance and properties very similar to **Ce**. It is prepared almost exclusively from cerite. By treating the mineral with an insufficient quantity of HNO_3, a solution rich in **La** may be obtained. The cerium is precipitated from the solution by alkali hypochlorite. The filtrate is converted into the sulphate and separated from **Ne** and **Pr** sulphates by fractional crystallization, the latter being more soluble (Holzman, *J. pr.*, 1858, **75**, 346). Fractional precipitation with NH_4OH is also used to separate **La** from **Ne** and **Pr**, the latter precipitating first (Cleve, *Bl.*, 1874, **21**, 196; 1883, **39**, 287). The metal is prepared from the chloride, $LaCl_3$, by electrolysis or by ignition with potassium. The ignition point of **La** is higher than that of **Ce**; it is also not so readily attacked by HNO_3. In cold water **La** is slowly attacked, but in hot water the action is violent (Winkler, *B.*, 1890, **23**, 787). With aluminium, lanthanum forms a crystalline white alloy which is stable in air and insoluble in nitric acid (Muthman and Beck, *A.*, **46**, 331, 1904.) The oxide, La_2O_3, is a white powder, readily soluble in acids; with water it forms the hydroxide, $La(OH)_3$, which reacts *alkaline* towards litmus and absorbs CO_2 from the air. $La(OH)_3$ is soluble in a solution of NH_4Cl (similar to $Mg(OH)_2$). The salts are colorless. K_2SO_4 and $H_2C_2O_4$ form precipitates with lanthanum salts as with cerium salts. **Fixed alkalis** precipitate lanthanum salts as $La(OH)_3$, white, insoluble in excess of the reagent and not changing color on exposure to the air (distinction from **Ce**). **Alkali carbonates** precipitate $La_2(CO_3)_3$, insoluble in excess. $BaCO_3$ precipitates the salts completely in the cold. NH_4OH precipitates basic salts. H_2S forms no precipitate; $(NH_4)_2S$ precipitates the *hydroxide*. Lanthanum gives a number of characteristic lines in the spark spectrum (Bettendorf, *A.*, 1889, **256**, 159).

§162. Neodymium. Nd = 144.3. See Didymium (§156).

§163. Praseodymium. Pr = 140.9. See Didymium (§156).

§164. Samarium. Sa = 150.4. Valence three.

Samarium was found in 1879 by Boisbaudran from didymium earths by its peculiar spectrum (*C. r.*, 1879, **88**, 323). According to Crookes, (*C. r.* 1886, **102**, 1464), it consists of at least two elements and is found in all yttrium earths. Its salts are light yellow, giving an absorption spectrum of six bands (Kruess, *B.*, 1887, **20**, 2144). In its chemical properties it is more similar to **Nd** and **Pr** than to **Y**. It is separated from **Nd** and **Pr** by the fractional precipitation of the hydroxide, basic nitrate, oxalate and sulphate; which separate before the corresponding **Nd** and **Pr** compounds. *Melting point*, 1300°–1400° (*Cir. B. of S.*, 1915).

§165. Scandium. Sc = 44.1. Valence three.

It is found in euxenite and gadolinite with yttrium. Its name comes from Scandinavia, where it was first found. It is separated from ytterbium, with which it is always closely associated, by heating the nitrates; the basic scandium nitrate being precipitated before the ytterbium basic nitrate, or by precipitating as the double potassium sulphate, the corresponding ytterbium

salt remaining in solution. The oxide, Sc_2O_3, is a white flocculent infusible powder, readily soluble in warm acids. The solutions of the salts show no absorption bands in the spectrum. The spark spectrum of the chloride gives over 100 bright lines (Thalen, *C. r.*, 1880, **91**, 45). Solutions of the salts taste sweet and have an astringent action. The **alkalis** precipitate the hydroxide, a white bulky precipitate, insoluble in excess of the precipitant. Tartrates hinder the precipitation in the cold, but not upon heating. Na_2CO_3 gives a bulky white precipitate, soluble in excess of the reagent. H_2S is without action, but $(NH_4)_2S$ precipitates the *hydroxide*. K_2SO_4 precipitates the double scandium sulphate, $3K_2SO_4.Sc_2(SO_4)_3$, soluble in water but not in a saturated K_2SO_4 solution.

§166. Tantalum. Ta = 181.5. Valence five.

Tantalum occurs in tantalite and columbite, silicates, nearly always accompanied by columbium. It is prepared by heating the tantalum alkali fluoride with **K** or **Na** in a well-covered crucible (Rose, *Pogg.*, 1856, **99**, 65). The electric furnace is now used in its preparation. It is a white metal, somewhat less bright than platinum and usually showing a bluish tarnish from superficial oxidation. *Specific gravity*, 16.8 (von Bolton). *Melting point*, 2850° (*Cir. B. of S.*, 1915). Wrought tantalum is about as hard as soft steel, but possesses a much greater tensile strength. When heated it becomes softer and can be hammered, rolled and drawn. Tantalum has become very important commercially on account of its high melting point, its property of hardening and improving steel, even when added in extremely small quantities, and its great acid-resisting properties. At a dull red heat tantalum absorbs large quantities of hydrogen and nitrogen, becoming brittle and generally changing its properties. The occluded gases may be removed by fusion *in vacuo* in the electric furnace. Heated in the air it burns with incandescence to form Ta_2O_5. It is insoluble in acid, including boiling aqua regia, except **HF**, in which it dissolves with evolution of **H**. Upon ignition in a current of chlorine, $TaCl_5$, volatile, is formed. Solution of alkalis has no action; upon fusion with the fixed alkalis an alkali tantalate is formed. Ta_2O_5 is a white infusible powder, specific gravity, 8.01 (Marignac, *A. Ch.*, 1866, (4), **9**, 254). The oxide fused with fixed alkalis gives also an alkali tantalate, $M'TaO_3$. When **KOH** is used, the fused mass is soluble in water. When **NaOH** is used, water removes the excess of alkali, leaving the $NaTaO_3$ as a white residue, which dissolves in pure water, but not in **NaOH** solution. Tantalum chloride is a yellow solid, melting at 211.3° and boiling at 241.6°, with 753 mm. atmospheric pressure (Deville and Troost, *C. r.*, 1867, **64**, 294). It is completely decomposed by water, forming the hydrated acid, $2HTaO_3.H_2O = H_4Ta_2O_7$. The freshly precipitated acid is soluble in acids and reprecipitated by NH_4OH. The acid is readily soluble in **HF**, which solution with **KF** forms a *characteristic* double salt, $2KF.TaF_5$, crystallizing in fine needles, insoluble in water slightly acidulated with **HF** (distinction and separation from columbium). A solution of alkali tantalate gives with **HCl** a precipitate of tantalic acid, soluble in excess of the **HCl**. From this solution NH_4OH or $(NH_4)_2S$ precipitates tantalic acid; H_2SO_4 precipitates tantalic sulphate. Tartaric acid prevents the precipitation with NH_4OH and $(NH_4)_2S$. A solution of tantalic acid gives no coloration with zinc (distinction from **Cb**). Solutions of alkali tantalates form tantalic acid with CO_2. The acid fused with sodium metaphosphate gives a colorless bead (distinction from SiO_2), which does not become blood-red upon adding $FeSO_4$ and heating in the inner flame (distinction from titanium).

§167. Terbium. Tb = 159.2. Valence three.

The terbium compounds are very similar to the yttrium compounds. The salts are colorless and give no absorption spectrum. The double potassium terbium sulphate has about the same solubilities as the corresponding cerium compound, and so the terbium is frequently precipitated with cerium compounds. Terbia, Tr_2O_3, is the darkest colored of the yttrium earths, soluble

in acids and sets NH_3 free from ammonium salts. The hydroxide is a gelatinous precipitate which absorbs CO_2 from the air. It is quite probable that terbia is a mixture of rare earths (Boisbaudran, *C. r.*, 1886, **102**, 153, 395, 483 and 899).

§168. Thallium. Tl = 204.00. Valence one and three.

Thallium was discovered by Crookes by means of the spectroscope in 1861, in selenium residues of the H_2SO_4 factory at Tilkerode in the Hartz Mountains, Germany (*C. N.*, 1861, **3**, 193, 303; 1863, **7**, 290; 1863, **8**, 159, 195, 219, 231, 243, 255 and 279). It is found widely distributed in many varieties of iron and copper pyrites, but in large proportions it is only found in Crookesite in Sweden. This mineral contains as high as 18.55 per cent Tl (Nordenskjoeld, *A.*, 1867, **144**, 127). It is prepared by reduction from its solutions with **Zn** or **Al**; by electrolysis; by precipitation with **KI**, and then reduction by **Zn** or **Al** or by electrolysis. *Specific gravity*, 11.85 (Petrenko, *Z. anorg.*, **50**, 133, 1906). *Melting point*, 302° (*Cir. B. of S.*, 1915). It is a bluish-white metal, softer than lead, malleable and ductile; tarnishes rapidly in the air; may be preserved under water, which it does not decompose below a red heat; soluble in H_2SO_4 and HNO_3, in **HCl** with great difficulty; combines directly with **Cl**, **Br**, **I**, **P**, **S**, **Se**, and precipitates from their solutions **Cu**, **Ag**, **Hg**, **Au** and **Pb** in the metallic state. As a monad its compounds are stable, and not easily oxidized; as a triad it is easily reduced to the univalent condition. **Thallious** oxide, Tl_2O, is black; on contact with water it forms an hydroxide, **TlOH**, freely soluble in water and in alcohol, to colorless solutions. The carbonate is soluble in about 20 parts of water; the sulphate and phosphate are soluble; the chloride very sparingly soluble; the iodide insoluble in water. **Hydrochloric acid** precipitates, from solutions not very dilute, *thallious chloride*, **TlCl**, white, and unalterable in the air. As a silver-group precipitate, thallious chloride dissolves enough in hot water to give the light yellow precipitate of *iodide*, **TlI**, on adding a drop of **potassium iodide** solution, the precipitate being slightly soluble in excess of the reagent. H_2S precipitates the acetate, but not the acidified solutions of its other salts. $(NH_4)_2S$ precipitates Tl_2S, which, on exposing to the air, soon oxidizes to sulphate. **Ferrocyanides** give a yellow precipitate, $Tl_4Fe(CN)_6$; **phosphomolybdic acid** a yellow precipitate; and potassium **permanganate** a red-brown precipitate, consisting in part of Tl_2O_3. **Chromates** precipitate yellow normal chromate; and **platinic chloride**, pale orange, *thallious platinic chloride*, Tl_2PtCl_6. Thallium compounds readily impart an intense green color to the **flame**, and one emerald-green line to the **spectrum** (the most delicate test). The flame-color and spectrum, from small quantities, are somewhat evanescent, owing to rapid vaporization. **Thallic** oxide, Tl_2O_3, dark violet, is insoluble in water; the hydroxide, an oxyhydroxide, **TlO(OH)**, is brown and gelatinous. This hydroxide is precipitated from thallic salts by the caustic **alkalis**, and not dissolved be excess. **Chlorides** and **bromides** do not precipitate thallic solutions; **iodides** precipitate **TlI** with **I**. **Sulphides** and H_2S precipitate *thallious sulphide*, with sulphur. Thallic oxide, suspended in solution of potassium hydroxide, and treated with **chlorine**, develops an intense violet-red color. Thallic chloride and sulphate are reduced to thallious salts by boiling their water solutions.

§169. Thorium. Th = 232.4. Valence four.

Thorium is a rare element found in thorite (a silicate), orangite, monazite, and some other minerals. It was described by Berzelius in 1828 (*Pogg.*, 1829, **16**, 385), who also prepared the metal by reduction of the potassium thorium fluoride with potassium. The metal is a gray powder; *specific gravity*, 11.000; *melting point*, >1700°, <1755° (*Cir. B. of S.*, 1915); stable in air at ordinary temperature, but igniting when heated; attacked by vapors of **Cl**, **Br**, **I** and **S**. Sparingly soluble in dilute acids, easily soluble in concentrated acids; insoluble in the alkalis (Nilson, *B.*, 1882, **15**, 2519 and 2537; Kruess

and Nilson, *B.*, 1887, **20**, 1665). Thorium forms one oxide, ThO_2, upon ignition of the oxalate. It is a snow-white powder, not easily soluble in acids if highly ignited (Cleve, *J.*, 1874, 261). The *hydroxide*, $Th(OH)_4$, is formed by precipitation of the salts by the **alkalis**. It is a white, heavy, gelatinous precipitate, drying to a hard glassy mass. The *chloride*, $ThCl_4$, and the *nitrate*, $Th(NO_3)_4$, are *deliquescent*. The *chloride* is a white body melting at a white heat and then subliming in beautiful white needles (Kruess and Nilson, *l. c.*). The *sulphate* is soluble in five parts of cold water. The *carbonate*, *oxalate* and *phosphate* are insoluble in water; the *oxalate* is scarcely soluble in dilute mineral acids. **Alkali hydroxides** or **sulphides** precipitate thorium hydroxide, $Th(OH)_4$, insoluble in excess of the reagent. Tartaric and citric acids hinder the precipitation. **Alkali carbonates** precipitate the basic carbonate, soluble in excess, if the reagent be concentrated. The solution in $(NH_4)_2CO_3$ readily reprecipitates upon warming. $BaCO_3$ precipitates thorium salts completely. **Oxalic acid** and **oxalates** form a white precipitate (distinction from **Al** and **Gl**), not soluble in oxalic acid or in dilute mineral acids; soluble in hot concentrated $(NH_4)_2C_2O_4$ and not reprecipitated on cooling and diluting (distinction from **Ce** and **La**). A saturated solution of K_2SO_4 slowly but completely precipitates a solution of $Th(SO_4)_2$, forming potassium thorium sulphate; *insoluble* in a saturated K_2SO_4 solution, sparingly soluble in cold water, readily soluble in hot water. **HF** precipitates ThF_4, insoluble in excess, gelatinous, becoming crystalline on standing. Boiling freshly precipitated $Th(OH)_4$ with **KF** in presence of **HF** forms $K_2ThF_6.4H_2O$, a heavy fine white precipitate almost *insoluble* in water. The *distinguishing* reactions of thorium are the *precipitation* with **oxalates** and with K_2SO_4, and failure to form a soluble compound on fusion with Na_2CO_3 (distinction from SiO_2 and TiO_2).

§170. Titanium. Ti = 48.1. Valence three and four.

Titanium is found quite widely distributed as rutile, brookite, anatase, titanite, titaniferous iron, $FeTiO_3$, and in many soils and clays. Never found native. It is prepared by heating the fluoride or chloride with **K** or **Na**. It is a dark gray powder, which shows distinctly metallic when *magnified*; *melting point*, 1800° (*Cir. B. of S.*, 1915). Heated in the air it burns with an unusually brilliant *incandescence*; sifted into the flame it burns with a *blinding brilliance*. Chlorine in the cold is without action, when heated it combines with vivid incandescence. It decomposes water at 100°. It is soluble in acids, with evolution of hydrogen, forming titanous salts. At a higher temperature it combines directly with **Br** and **I**. It is almost the *only metal* that combines *directly* with *nitrogen* when heated in the air (Woehler and Deville, *A.*, 1857, **103**, 230; Merz, *J. pr.*, 1866, **99**, 157). The most common oxide of titanium is the dioxide, TiO_2, analogous to CO_2 and SiO_2. It occurs more or less pure in nature as rutile, brookite and anatase; it is formed by ignition of the hydrated titanic acid or of ammonium titanate (Woehler, *J.*, 1849, 268). Ignition of TiO_2 in dry hydrogen gives Ti_2O_3, an amorphous black powder, dissolving in H_2SO_4 to a violet-colored solution (Ebelmen, *A. Ch.*, 1847, (3), **20**, 392). **TiO** is formed when TiO_2 is ignited with **Mg**: $2TiO_2 + Mg = TiO + MgTiO_3$ (Winkler, *B.*, 1890, **23**, 2660). Other oxides have been reported. **Titanic acid**, TiO_2, is a white powder, melts somewhat easier than SiO_2, soluble in the alkalis unless previously strongly ignited. Mixed with charcoal and heated in a current of chlorine, $TiCl_4$ is formed. The bromide is formed in a similar manner. TiO_2 acts as a *base*, forming a series of stable salts; also as an *acid*, forming titanates. $TiCl_4$ is a colorless liquid, fuming in the air; it boils at 136.41° (Thorpe, *J. C.*, 1880, **37**, 329); it is decomposed by *water*, forming titanic acid, which remains in solution in the **HCl** present. Solutions of most of the titanic salts, when boiled, deposit the insoluble meta-titanic acid. **HF** dissolves *all* forms of titanic acid; if the solution be evaporated in presence of H_2SO_4 no TiF_4 is volatilized (distinction from SiF_4). When evaporated with **HF** alone, TiF_4 is volatilized. The double *potassium titanium fluoride*, K_2TiF_6, formed by fusing TiO_2 with acid **KF**, is sparingly soluble in water (96 parts), readily soluble in **HCl**. Solutions of titanic salts in water or acid solutions of titanic acid are precipitated by **alkali hydroxides, carbonates** and *sulphides* as the *hydrated titanic acid*, insoluble in excess of the precipitants and in ammonium salts. $BaCO_3$ gives the same

precipitate. $K_4Fe(CN)_6$ gives a reddish-yellow precipitate; $K_3Fe(CN)_6$ a yellow precipitate. Na_2HPO_4 precipitates the titanium *almost completely*, even in the presence of strong **HCl**. An acid solution of TiO_2 when treated with **Sn** or **Zn** gives a *pale blue* to *violet coloration* to the solution, due to a partial *reduction* of the titanium to the triad condition. These colored solutions are precipitated by **alkali hydroxides, carbonates** and **sulphides**. H_2S is without action. The solution reduces **Fe‴** to **Fe″**, **Cu″** to **Cu′**, and salts of **Hg**, **Ag** and **Au** to the metallic state; the titanium becoming again the tetrad. The reduction by **Sn** or **Zn** takes place in presence of **HF** (distinction from columbic acid). Titanium compounds fused in the flame with microcosmic salt give in the reducing flame a yellow bead when hot, cooling to reddish and violet (reduction of the titanium). With $FeSO_4$ in the reducing flame a *blood-red bead* is obtained.

Titanium is very readily detected in minerals as follows. 0.1 gram of the finely powdered mineral is mixed with 0.2 gram of finely powdered sodium fluoride and 3 grams sodium pyrosulphate added without mixing. The crucible is heated until copious sulphuric acid fumes are evolved. The fused mass is rapidly cooled and heated with 2–3 c.c. dilute sulphuric acid and 10 c.c. water added. The solution is divided into two parts and a few drops of hydrogen peroxide added to one part. A yellow color is produced by the titanium. Chlorides, bromides and iodides interfere with this very delicate reaction (Weber, *Z.*, **40**, 799, Noyes, *J. Soc. Ind.*, **10**, 485).

§171. Uranium. U = 238.2. Valence four and six.

Specific gravity, 18.685 (Zimmermann, *A.*, 1882, **213**, 285). *Melting point*, <1850° (*Cir. B. of S.*, 1915). Found in various minerals; its chief ore is pitch-blende, which contains from 40 to 90 per cent of U_3O_8. Prepared by fusing UCl_4 with **K** or **Na** (Zimmermann, *A.*, 1883, **216**, 1; 1886, **232**, 273). It has the color of nickel, hard, but softer than steel, malleable, permanent in the air and water at ordinary temperatures; when ignited burns with incandescence to U_3O_8; unites directly with **Cl**, **Br**, **I** and **S** when heated; soluble in **HCl**, H_2SO_4 and slowly in HNO_3. *Uranous oxide*, UO_2, formed by igniting the higher oxides in carbon or hydrogen, is a brown powder, soon turning yellow by absorption of oxygen from the air. *Uranous hydroxide* is formed by precipitating uranous salts with alkalis. *Uranic oxide*, UO_3, is formed by heating uranic nitrate cautiously to 25°, and upon ignition in the air both this and other uranium oxides, hydroxides and uranium oxysalts with volatile acids are converted into $U_3O_8 = UO_2{\cdot}2UO_3$. Uranium acts as a base in two classes of salts, *uranous* and *uranyl* salts. *Uranous* salts are green and give green solutions, from which alkalis precipitate uranous hydroxide, insoluble in excess of the alkali; alkali carbonates precipitate $U(OH)_4$, soluble in $(NH_4)_2CO_3$; with $BaCO_3$ the precipitation is complete even in the cold. H_2S is without action; $(NH_4)_2S$ gives a dark-brown precipitate; $K_4Fe(CN)_6$ gives a reddish-brown precipitate. In their action toward oxidizing and reducing agents uranous and uranyl (uranic) salts resemble closely ferrous and ferric salts; uranous salts are even more easily oxidized than ferrous salts, *e. g.*, by exposure to the air, by HNO_3, **Cl**, $HClO_3$, **Br**, $KMnO_4$, etc. Gold, silver and platinum salts are reduced to the free metal. The hexad uranium (U^{VI}) acts as a base, but usually forms basic salts, never normal: we have $UO_2(NO_3)_2$, not $U(NO_3)_6$; UO_2SO_4, not $U(SO_4)_3$. These basic salts were formerly called uranic salts, but at present $(UO_2)''$ is regarded as a basic radical and called *uranyl*, and its salts are called uranyl salts, *e. g.*, UO_2Cl_2 uranyl chloride, $(UO_2)_3(PO_4)_2$ uranyl orthophosphate. Solutions of uranyl salts are yellow; **KOH** and **NaOH** give a yellow precipitate, uranates, $K_2U_2O_7$ and $Na_2U_2O_7$, insoluble in excess. Alkali carbonates give a yellow precipitate, soluble in excess; $BaCO_3$ and $CaCO_3$ give UO_3. H_2S does not precipitate the uranium, but slowly reduces uranyl salts to uranous salts (Formanek, *A.*, 1890, **257**, 115). $(NH_4)_2S$ gives a dark-brown precipitate. $K_4Fe(CN)_6$ gives a reddish-brown precipitate. Used in the analysis and separation of uranium compounds (Fresenius and Hintz, *Z. angew.*, 1895, 502). Sodium phosphate gives a yellow precipitate. The hexad uranium acts as an acid toward some stronger bases.

Thus we have $K_2U_2O_7$ and $Na_2U_2O_7$, formed by precipitating uranyl salts with **KOH** and **NaOH**; compare the similar salts of the hexad chromium, $K_2Cr_2O_7$ and $Na_2Cr_2O_7$. Other oxides of uranium are described, but are doubtless combinations of UO_2 and UO_3. **Zn**, **Cd**, **Sn**, **Pb**, **Co**, **Cu**, **Fe**, and ferrous salts reduce uranyl salts to uranous salts. Solutions of **Sn**, **Pt**, **Au**, **Cu**, **Hg** and **Ag** are reduced to the metal by metallic uranium (Zimmermann, *l. c.*). For method of recovery of waste uranium compounds, see Laube (*Z. angew.*, 1889, 575).

§171a. Vanadium. V = 51.0. Valence two to five.

1. **Properties.**—*Specific gravity*, 5.8 (Moissan, *C. r.*, **122**); *melting point* 1720° (*Cir. B. S.*, **35**, 1915). A grayish non-magnetic powder; slowly oxidized in the air, rapidly on ignition with formation of V_2O_5. It forms with chlorine the dark brown tetrachloride.

2. **Occurrence.**—It is often found in iron and copper ores and in some clays and rare minerals, *e.g.*, vanadinite, $(Pb_5Cl(VO_4)_3)$; volborthite, $(Cu,Ca,Ba)_3(OH)_3VO_4 + 6H_2O)$; mottramite (a hydrous vanadate of lead, copper, and other divalent elements, of uncertain formula, $(R_3(VO_4)_2.3R(OH)_2))$.

3. **Preparation.**—The vanadium ores are treated chiefly for the preparation of ammonium vanadate and vanadic acid. The ores are fused with KNO_3, forming potassium vanadate. This is precipitated with **Pb** or **Ba** salts and then decomposed with H_2SO_4. The vanadic acid is neutralized with NH_4OH and precipitated with NH_4Cl, in which it is insoluble. This upon ignition gives V_2O_5 pure (Wöhler, *A.*, 1851, **78**, 125). The metal is prepared from the dichloride, VCl_2, by long-continued ignition in a current of hydrogen.

4. **Oxides.**—Vanadium forms four oxides: VO, gray; V_2O_3, black; VO_2, dark blue; and V_2O_5, dark red to orange red.

5. **Solubilities.**—Vanadium is not attacked by dilute **HCl** or H_2SO_4; concentrated H_2SO_4 gives a greenish-yellow solution; HNO_3 a blue solution. VO dissolves in acids to a blue solution with evolution of hydrogen. V_2O_3 dissolves in dilute **HCl** to a dark greenish-black solution. Chlorine forms with V_2O_3, $VOCl_3$ and V_2O_5. VO_2 dissolves in acids to a blue solution, from which solutions Na_2CO_3 gives a precipitate of $V_2O_2(OH)_4 + 5H_2O$, grayish-white mass, losing $4H_2O$ at 100° and turning black, soluble in acids and alkalis. V_2O_5 exists in several modifications with different solubilities in water, the red modification being soluble in 125 parts of water at 20° (Ditte, *C. r.*, 1880, **101**, 698). Vanadic acid forms three series of salts, ortho, meta and pyro, analogous to the phosphates. Most salts are the metavanadates. The ortho compounds are quite unstable, readily changed to the meta and pyro compounds. Alkali vanadates are soluble in water, the ammonium vanadate least soluble and not at all in NH_4Cl.

6. **Reactions.**—Solutions of vanadic acid produce brown precipitates with alkalis, soluble in excess to a yellowish-brown color. Potassium ferrocyanide gives a green precipitate, insoluble in acids. Tannic acid gives a blue-black solution, which is said to make a desirable ink. Ammonium sulphide precipitates V_2S_5, brown, soluble with some difficulty in excess of the reagent to a reddish-brown thio salt. From this solution acids reprecipitate the brown vanadic sulphide, V_2S_5.

If to a solution of a vanadate, neutral or alkaline, solid NH_4Cl be added, the vanadium is completely precipitated as NH_4VO_3, ammonium metavanadate, crystalline, colorless, insoluble in NH_4Cl solution; upon ignition in air or oxygen, pure vanadic oxide, V_2O_5, is obtained.

7. **Ignition.**—Borax gives with vanadium compounds in the outer flame a colorless bead, yellow if much vanadium be present; in the inner flame a green bead, or brown when vanadium is present in large quantities and hot, becoming green upon cooling. All the lower oxides of vanadium ignited in air or oxygen give V_2O_5.

8. **Detection.**—Vanadium will almost always be found as a vanadate (2) and is detected by the reactions used in its purification (3); also by the reactions with reducing agents, forming the colored lower oxidized compounds (10).

9. **Estimation.**—(*1*) It is precipitated as basic lead vanadate and dried at 100°. (*2*) It is precipitated as ammonium vanadate, NH_4VO_3, in strong NH_4Cl solution, ignited to the oxide V_2O_5, and weighed.

10. **Oxidation.**—**Zn**, in solutions of vanadates with dilute H_2SO_4, reduces the vanadium to the tetrad, a green to blue solution, then greenish-blue to green, the triad, and finally to lavender blue, the dyad. H_2S reduces vanadates to the tetrad with separation of sulphur. Oxalic acid and sulphurous acid also reduce vanadates to the tetrad, the solution becoming blue.

§172. Ytterbium. Yb = 173.5. Valence three.

Obtained as an earth by Marignac (*C. r.*, 1878, **87**, 578) from a gadolinite earth; by Delafontaine (*C. r.*, 1878, **87**, 933) from sipylite found at Amherst, Va. Nilson (*B.*, 1879, **12**, 550; 1880, **13**, 1433) describes its preparation from euxenite and its separation from **Sc**. It has the lowest bacisity of the yttrium earths. The double **potassium ytterbium sulphate** is easily soluble in water and in potassium sulphate. The **oxalate** forms a white crystalline precipitate, insoluble in water and in dilute acids. The salts are colorless and give no absorption spectrum. For the spark spectrum see Welsbach (*M.*, 1884, **5**, 1). The *oxide*, Yb_2O_3, is a white powder, slowly soluble in cold acids, readily upon warming. The *hydroxide* forms a gelatinous precipitate, insoluble in NH_4OH but soluble in **KOH**. It absorbs CO_2 from the air. The *nitrate* melts in its water of crystallization and is very soluble in water.

§173. Yttrium. Y = 88.7. Valence three.

Yttrium is one of the numerous rare metals found in the gadolinite mineral at Ytterby, near Stockholm, Sweden; also found in Colorado (Hidden and Mackintosh, *Am. S.*, 1889, **38**, 474). The metal has been prepared by electrolysis of the chloride; also by heating the oxide, Y_2O_3, with **Mg** (Winkler, *B.*, 1890, **23**, 787). *Melting point*, 1490° (*Cir. B. of S.*, 1915). The study of these rare earths is by no means complete. It is also claimed that they have not yet been obtained pure, but that the so-called pure oxides really consist of a mixture of oxides of from five to twenty elements (Crookes, *C. N.*, 1887, **55**, 107, 119 and 131). The most of these rare earths do not give an absorption spectrum, but give *characteristic* spark spectra; and it is largely by this means that the supposedly pure oxides have been shown to be mixtures of the oxides of several closely related elements (Welsbach, *M.*, 1883, **4**, 641; Dennis and Chamot, *J. Am. Soc.*, 1897, **19**, 799). Yttrium salts are precipitated by the **alkalis** and by the **alkali sulphides** as the *hydroxide*, $Y(OH)_3$, a white bulky precipitate, insoluble in the excess of the reagents (distinction from **Gl**). The *oxide* and *hydroxide* are readily soluble in acids; boiling with NH_4Cl causes solution of the *hydroxide* as the *chloride*. The **alkali carbonates** precipitate the carbonate $Y_2(CO_3)_3$, soluble in a large excess of the reagents. If the solution in ammonium carbonate be boiled, the *hydroxide* is precipitated. Soluble **oxalates** precipitate yttrium salts as the white oxalate (distinction from **Al** and **Gl**); soluble with some difficulty in **HCl**. The double sulphate with potassium is soluble in water and in potassium sulphate (distinction from thorium, zirconium and the cerite metals). $BaCO_3$ forms no precipitate in the cold (distinction from **Al**, Fe''', Cr''', **Th**, **Ce**, **La**, **Nd** and **Pr**). **Hydrofluoric acid** precipitates the gelatinous *fluoride*, YF_3, insoluble in water and in **HF**. The precipitation of yttrium salts is not hindered by the presence of tartaric acid (distinction from **Al**, **Gl**, **Th** and **Zr**). The analysis of yttrium usually consists in its detection and separation in gadolinite (silicate of **Y**, **Gl**, **Fe**, **Mn**, **Ce** and **La**). Fuse with alkali carbonate, decompose with **HCl**, and filter from the SiO_2. Neutralize the filtrate and precipitate the **Y**, **La** and **Ce** as oxalates with $(NH_4)_2C_2O_4$. Ignite the precipitate and dissolve in **HCl**. Precipitate the **La** and **Ce** as the double potassium sulphates, and from the filtrate precipitate the yttrium as the hydroxide with NH_4OH. Ignite and weigh as the oxide. In order to effect complete separations the operations should be repeated several times.

§174. Zirconium. Zr = 90.6. Valence four.

Zirconium is a rare metal found in various minerals, chiefly in zircon, a silicate; never found native. The metal was first prepared by Berzelius in 1824 by fusion of the potassium zirconium fluoride with potassium (*Pogg.*, 1825, **4**, 117). Also prepared by electrolysis of the chloride (Becquerel, *A. Ch.*, 1831, **48**, 337). *Melting point*, 1700° ? (*Cir. B. of S.*, 1915). The metal exists in three modifications: crystalline, graphitoidal and amorphous. The amorphous zirconium is a velvet-black powder, burning when heated in the air. Acids attack it slowly even when hot, except **HF**, which dissolves it in the cold. It forms but one oxide, ZrO_2, analogous to SiO_2 and TiO_2. ZrO_2 is prepared from the mineral zircon by **fusion** with a **fixed alkali.** Digestion in water removes the most of the silicate, leaving the *alkali zirconate* as a sandy powder. Digestion with **HCl** precipitates the last of the SiO_2 and dissolves the zirconate. The solution is neutralized, strongly diluted and boiled, whereupon the zirconium precipitates as the basic chloride free from iron. Or the zirconium may be precipitated by a saturated solution of K_2SO_4, and after resolution in acids precipitated by NH_4OH and ignited to ZrO_2 (Berlin, *J. pr.*, 1853, **58**, 145; Roerdam, *C. C.*, 1889, 533). ZrO_2 is a white infusible powder, giving out an **intense white light** when heated; it shows no lines in the spectrum. It is much used with other rare earths, La_2O_3, Y_2O_3, etc., to form the *mantles* used in the *Welsbach gas-burners* (Drossbach, *C. C.*, 1891, 772; Welsbach, *J.*, 1887, 2670; *C. N.*, 1887, **55**, 192). The *oxide* (or hydroxide precipitated hot) dissolves with difficulty in acids to form salts. The *hydroxide*, $ZrO(OH)_2$, precipitated in the cold dissolves readily in acids. As an *acid*, zirconium hydroxide, $ZrO(OH)_2 = H_2ZrO_3$, forms zirconates, decomposed by acids. As a *base* it forms zirconium salts with acids. The *sulphate* is easily soluble in water, crystallizing from solution with $4H_2O$. The *phosphate* is insoluble in water, formed by precipitation of zirconium salts by Na_2HPO_4 or H_3PO_4. The *silicate*, $ZrO_2.SiO_2$, is found in nature as the mineral zircon, usually containing traces of iron. *Zirconium chloride* is formed when a current of chlorine is passed over heated ZrO_2, mixed with charcoal. It is a white solid, may be sublimed, is soluble in water. Solutions of zirconium salts are precipitated as the hydroxide, $ZrO(OH)_2$, by **alkali hydroxides** and **sulphides**, a white flocculent precipitate, insoluble in excess of the reagents, insoluble in NH_4Cl solution (difference from **Gl**). Tartaric acid prevents the precipitation. **Alkali carbonates** precipitate basic zirconium carbonate, white, soluble in excess of $KHCO_3$ or $(NH_4)_2CO_3$; boiling precipitates a gelatinous hydroxide from the latter solution. $BaCO_3$ does not precipitate zirconium salts completely, even on boiling. The precipitates of the hydroxide and carbonate are soluble in acids. **Oxalic acid** and **oxalates** precipitate zirconium oxalate, soluble in excess of oxalic acid on warming, and soluble in the cold in $(NH_4)_2C_2O_4$ (difference from thorium); soluble in **HCl**. A saturated solution of K_2SO_4 precipitates the double *potassium zirconium sulphate*, white, insoluble in excess of the reagent if precipitated cold, soluble in excess of **HCl**; if precipitated hot, almost absolutely insoluble in water or **HCl** (distinction from **Th** and **Ce**). Zirconium salts are precipitated on warming with $Na_2S_2O_3$ (separation from **Y**, **Nd** and **Pr**). Solution of H_2O_2 completely precipitates zirconium salts. *Tumeric paper* moistened with a solution of zirconium salt and **HCl** is colored *orange* upon drying (boric acid gives the same reaction) (Brush, *J. pr.*, 1854, **62**, 7). **HF** does not precipitate zirconium solutions, as zirconium fluoride, ZrF_4, is soluble in water and in **HF** (distinction from **Th** and **Y**).

The Calcium Group (Fifth Group).—(The Alkaline Earth Metals.)

Barium. Ba = 137.37. **Calcium.** Ca = 40.07.
Strontium. Sr = 87.63. **Magnesium.** Mg = 24.32.

§175. Like the alkali metals, **Ba**, **Sr**, and **Ca oxidize** rapidly in the air at ordinary temperatures—forming **alkaline earths**—and *decompose water*, forming **hydroxides** with evolution of heat. **Mg** oxidizes rapidly in the air

when ignited, decomposes water at 100°, and its oxide—in physical properties farther removed from **Ba**, **Sr**, and **Ca** than these oxides are from each other—slowly unites with water without sensible production of heat. As compounds, these metals are not easily oxidized beyond their quantivalence as dyads, and they require very strong reducing agents to restore them to the elemental state.

§176. In *basic power*, **Ba** is the strongest of the four, **Sr** somewhat stronger than **Ca**, and **Mg** much weaker than the other three. It will be observed that the *solubility* of their *hydroxides* varies in the *same* decreasing **gradation**, which is also that of their atomic weights; while the solubility of their *sulphates* varies in a *reverse* order, as follows: (§7):

§177. The *hydroxide* of **Ba** **dissolves** in about 30 parts of water; that of **Sr**, in 100 parts; of **Ca**, in 800 parts; and of **Mg**, in 100,000 parts. The *sulphate* of **Ba** is not appreciably soluble in water (429,700 parts at 18.4°; Hollemann, *Z. phys. Ch.*, 1893, **12**, 131); that of **Sr** dissolves in 10,000 parts; of **Ca**, in 500 parts; of **Mg**, in 3 parts. To the extent in which they dissolve in water, alkaline earths render their solutions **caustic** to the taste and touch, and alkaline to **test-papers** and phenolphthalein.

§178. The carbonates of the alkaline earths are not entirely insoluble in pure water: $BaCO_3$ is soluble in 45,566 parts at 24.2° (Hollemann, *Zeit. phys. Ch.*, 1893, **12**, 125); $SrCO_3$ in 90,909 parts at 18° (Kohlrausch and Rose, *Zeit. phys. Ch.*, 1893, **12**, 241); $CaCO_3$ in 80,040 parts at 23.8° (Hollemann, *l. c.*); $MgCO_3$ in 9,434 parts (Chevalet, *Z.*, 1869, **8**, 91). The presence of NH_4OH and $(NH_4)_2CO_3$ lessens the solubility of the carbonates of **Ba**, **Sr**, and **Ca**, while their solubility is increased by the presence of NH_4Cl. $MgCO_3$ is soluble in ammonium carbonate and in ammonium chloride, so much so that in presence of an abundance of the latter it is not at all precipitated by the former, *i. e.* $(NH_4)_2CO_3$ does not precipitate a solution of $MgCl_2$ as the NH_4Cl formed holds the **Mg** in solution.

§179. These metals may be all precipitated as phosphates in presence of ammonium salts, but their further separation for identification or estimation would be attended with difficulty (§145 and *ff.*).

§180. The oxalates of **Ba**, **Sr**, and **Mg** are sparingly soluble in water, calcium oxalate insoluble. Barium chromate is insoluble in water (§§27 and 186, 5*c*), strontium chromate sparingly soluble, and calcium and magnesium chromates freely soluble.

§181. In qualitative analysis, **the group-separation** of the fifth-group metals is effected, after removal of the first four groups of bases, by precipitation with carbonate in presence of ammonium chloride, after which magnesium is precipitated from the filtrate, as phosphate.

§182. The **hydroxides** of **Ba**, **Sr**, and **Ca**, in their saturated solutions, necessarily dilute, precipitate solutions of salts of the metals of the first

four groups and of **Mg**, as hydroxides. In turn, the **fixed alkalis** precipitate, from solutions of **Ba**, **Sr**, **Ca**, and **Mg**, so much of the hydroxides of these metals as does not dissolve in the water present *; but *ammonium hydroxide* precipitates only **Mg**, and this but in part, owing to the solubility of $Mg(OH)_2$ in ammonium salts.

§183. Solutions containing **Ba**, **Sr**, **Ca**, and **Mg**, *and phosphoric, oxalic,* boric, or arsenic acid, necessarily have an acid reaction, because these phosphates, oxalates, etc., are soluble only in acids; such solutions are *precipitated by ammonium hydroxide* or by any agent which *neutralizes* the solution, and, consequently, we have precipitates of this kind in the **third group** (§145 and *ff.*):

$$CaCl_2 + H_3PO_4 + 2NH_4OH = CaHPO_4 + 2NH_4Cl + 2H_2O$$
$$CaH_4(PO_4)_2 + 2NH_4OH = CaHPO_4 + (NH_4)_2HPO_4 + 2H_2O.$$

If excess of the ammonium hydroxide be added the precipitate is $Ca_3(PO_4)_2$. Barium and strontium react like calcium. In the case of a magnesium salt the precipitate is $MgNH_4PO_4$.

§184. The *carbonates* of the alkaline earth metals are dissociated by heat, leaving metallic oxides and carbonic anhydride. This occurs only at a high temperature in the case of **Ba**.

§185. Compounds of **Ba**, **Sr**, and **Ca** (preferably with **HCl**) impart characteristic colors to the non-luminous **flame**, and readily present well-defined **spectra**.

§186. Barium. Ba=137.37. Valence two.

1. **Properties.**—*Specific gravity*, 3.75 (Kern, *C. N.*, 1875, **31**, 243); *melting point*, 850° (*Cir. B. of S.*, 1915). It is a white metal, stable in dry air, but readily oxidized in moist air or in water at ordinary temperature, hydrogen being evolved and barium hydroxide formed. It is malleable and ductile (Kern, *l. c.*).

2. **Occurrence.**—Barium can never occur in nature as the metal or oxide, or hydroxide near the earth's surface, as the metal oxidizes so readily, and the oxide and hydroxide are so basic, absorbing acids readily from the air. Its most common forms of occurrence are barite, $BaSO_4$, and witherite, $BaCO_3$.

3. **Preparation.**—(*1*) By electrolysis of the chloride fused or moistened with strong **HCl**. (*2*) By electrolysis of the carbonate, sulphate, etc., mixed with **Hg** and **HgO**, and then distilling the amalgam. (*3*) By heating the oxide or various salts with sodium or potassium and extracting the metal formed with mercury, then separating by distillation of the amalgam.

4. **Oxides** and **Hydroxides.**—The oxide, **BaO**, is formed by the action of heat upon the hydroxide, carbonate, nitrate, oxalate, and all its organic salts. The corresponding hydroxide, $Ba(OH)_2$, is made by treating the oxide with water. The peroxide, BaO_2, is made by heating the oxide almost to redness in oxygen, or air which has been freed from carbon dioxide; by heating the oxide with potassium chlorate (Liebig, *Pogg.*, 1832, **26**, 172) or cupric oxide (Wanklyn, *B.*, 1874, **7**, 1029). It is used as a source of oxygen, which it gives off at a white heat, **BaO** remaining; also in the manufacture of hydrogen peroxide, H_2O_2, which is formed by treating it with dilute acids: $BaO_2 + 2HCl = BaCl_2 + H_2O_2$.

* The presence of an excess of fixed alkali renders these hydroxides much less soluble, the high concentration of the hydroxyl ions, one of the factors of the solubility product, diminishing the other factor. (§45).

5. **Solubilities.**—*a.—Metal.*—Metallic barium is readily soluble in acids with evolution of hydrogen. *b.—Oxides* and *hydroxides.*—Barium oxide is acted upon by water with evolution of heat and formation of the hydroxide, which is soluble in about 30 parts of cold water and in its own weight of hot water (Rosenstheil and Ruehlmann, *J.*, 1870, 314). Barium peroxide, BaO_2, is very sparingly soluble in water (Schöne, *A.*, 1877, **192**, 257); soluble in acids with formation of H_2O_2.

c.—Salts.—Most of the soluble salts of barium are permanent: the acetate is efflorescent. The chloride, bromide, bromate, iodide, sulphide, ferrocyanide, nitrate, hypophosphite, chlorate, acetate, and phenylsulphate, are freely soluble in water; the carbonate, *sulphate*, sulphite, *chromate*,* phosphite, phosphate, oxalate, iodate, and *silico-fluoride*, are insoluble in water. The sulphate is perceptibly soluble in strong **HCl**. The chloride is almost insoluble in strong hydrochloric acid (separation from **Ca** and **Mg**) (Mar, *Am. S.*, 1892, **143**, 521); likewise the nitrate in strong hydrochloric and nitric acids. The chloride and nitrate are insoluble in alcohol.

6. **Reactions.** *a.*—The **fixed alkali hydroxides** precipitate only concentrated solutions of barium salts (5*b*). No precipitate is formed with **ammonium hydroxide** (§45). The **alkali carbonates** precipitate barium carbonate, $BaCO_3$, white. The precipitation is promoted by heat and by ammonium hydroxide, but is made slightly incomplete by the presence of ammonium salts (Vogel, *J. pr.*, 1836, **7**, 455).

Barium Carbonate—$BaCO_3$—is a valuable **reagent** for special purposes, chiefly for separation of third and fourth group metals. It is used in the form of the moist precipitate, which must be thoroughly washed. It is best precipitated from boiling solutions of barium chloride and sodium or ammonium carbonate, washed once or twice by decantation, then by filtration, till the washings no longer precipitate solution of silver nitrate. Mixed with water to consistence of cream, it may be preserved for some time in stoppered bottles, being shaken whenever required for use. When dissolved in hydrochloric acid, and fully precipitated by sulphuric acid, the filtrate must yield no fixed residue. This **reagent** removes sulphuric acid (radical) from all sulphates in solution to which it is added (*c*): $Na_2SO_4 + BaCO_3 = BaSO_4 + Na_2CO_3$. When salts of non-alkali metals are so decomposed, of course, they are left insoluble, as carbonates or hydroxides, nothing remaining in solution:

$$FeSO_4 + BaCO_3 = BaSO_4 + FeCO_3$$
$$Fe_2(SO_4)_3 + 3BaCO_3 + 3H_2O = 3BaSO_4 + 2Fe(OH)_3 + 3CO_2$$

The chlorides of the third group, except Fe'', are decomposed by barium carbonate; while the metals of the fourth group (zinc, manganese, cobalt, nickel), are not precipitated from their chlorides by this reagent. Tartaric

* Kohlrausch and Rose, *Z. phys. Ch.*, 1893, **12**, 241; Schweitzer, *Z.*, 1890, **29**, 414.

acid, citric acid, sugar, and other organic substances, hinder or prevent the decomposition by barium carbonate.

b.—**Ammonium oxalate** precipitates barium oxalate, BaC_2O_4, from solutions of barium salts, sparingly soluble in water, more soluble in presence of ammonium chloride; soluble in oxalic and acetic acids (Souchay and Lenssen, *A.*, 1856, **99**, 36).

c.—Solutions of barium salts are precipitated by the addition of concentrated **nitric acid** (5*c*). *d.*—Soluble **phosphates**, full metallic, or two-thirds metallic, as Na_2HPO_4, precipitate barium phosphate, white, consisting of $BaHPO_4$ when the reagent is two-thirds metallic, and $Ba_3(PO_4)_2$ when the reagent is full metallic. Soluble **phosphites** precipitate barium salts, **hypophosphites** do not. *e.*—Barium sulphide is not formed in the wet way, hence **hydrosulphuric acid** and soluble **sulphides** are without action upon barium salts. Soluble **sulphites** precipitate solutions of barium salts as barium sulphite, $BaSO_3$, insoluble in water but soluble in hydrochloric acid (distinction from sulphates).

Sulphuric acid, H_2SO_4, and all soluble **sulphates**, precipitate *barium sulphate* ($BaSO_4$), white, very soluble in hot concentrated sulphuric acid. *Immediate* precipitation by the (dilute §**188**, 5*c*) saturated solution of calcium sulphate distinguishes **Ba** from **Sr** (and of course from **Ca**); but precipitation by the (very dilute §**187**, 5*c*) solution of strontium sulphate is a more certain test between **Ba** and **Sr**. $BaSO_4$ is not transposed by solutions of alkali carbonates (distinction from **Sr** and **Ca**, §**188**, 6*a* footnote).

f.—Solutions of **iodates**, as $NaIO_3$, precipitate, from barium solutions not very dilute, barium iodate, $Ba(IO_3)_2$, white, soluble in 600 parts of hot or 1746 parts of cold water (distinction from the other alkaline earth metals). *g.*—Neutral or ammoniacal solutions of **arsenous** acid do not precipitate barium salts (distinction from calcium). Soluble **arsenates** precipitate solutions of barium salts, soluble in acids, including arsenic acid.

h.—Soluble **chromates**, as K_2CrO_4, precipitate solutions of barium salts as barium chromate, $BaCrO_4$, yellow; almost insoluble in water (separation from calcium and from strontium except in concentrated solutions), sparingly soluble in acetic acid, moderately soluble in chromic acid and readily soluble in hydrochloric and nitric acids. Bichromates, as $K_2Cr_2O_7$, precipitate solutions of barium salts (better from the acetate) as the normal chromate (very accurate separation from strontium and calcium) (Grittner, *Z. angew.*, 1892, 73).

i.—**Fluosilicic acid**, H_2SiF_6, precipitates white, crystalline barium fluosilicate, $BaSiF_6$, slightly soluble in water (1-4000), not soluble in alcohol (distinction from strontium and calcium). If an equal volume of alcohol be added the precipitation is complete, sulphuric acid not giving a precipitate in the filtrate (Fresenius, *Z.*, 1890, **29**, 143).

7. **Ignition.**—The volatile salts of barium as the chloride or nitrate impart a yellowish-green color to the flame of the Bunsen burner, appearing blue when viewed through a green glass. The spectrum of barium is readily distinguished from the spectra of other metals by the green bands Ba α, β and γ. Barium carbonate is very stable when heated, requiring a very high heat to decompose it into **BaO** and CO_2.

8. **Detection.**—In the filtrate from the fourth group, barium is precipitated with strontium and calcium as the carbonate by ammonium carbonate. The white precipitate (well washed) is dissolved in acetic acid and the barium precipitated with $K_2Cr_2O_7$ as $BaCrO_4$ which separates it from strontium and calcium. The barium is further identified by the non-solubility of the chromate in acetic acid, the solubility in hydrochloric acid, and precipitation from this solution by sulphuric acid. It may also be confirmed by the color of the flame with any of the volatile salts (7) (not the sulphate).

9. **Estimation.**—Barium is weighed as a sulphate (Fresenius and Hurtz, *Z. angew.*, 1896, 253), carbonate or fluosilicate ($BaSiF_6$). It is separated from strontium and calcium: (*1*) By digesting the mixed sulphates at ordinary temperatures for 12 hours with ammonium carbonate. The calcium and strontium are thus converted into carbonates, which are separated from the barium sulphate by dissolving in hydrochloric acid. (*2*) By hydrofluosilicic acid. (*3*) By repeated precipitation as the chromate in an acetate solution.

It is separated from calcium by the solution of the nitrate of the latter in amyl alcohol (§188, 9). The hydroxide and carbonates are also determined by alkalimetry. Volumetrically it is precipitated as the chromate, thoroughly washed, dissolved in dilute **HCl** and the Cr^{VI} determined by H_2O_2 (Baumann, *Z. angew.*, 1891, 331).

10. **Oxidation.**—Barium compounds are reduced to the metal when heated with **Na** or **K** (3). BaO_2 oxidizes $MnCl_2$ to Mn_2O_3 (Spring and Lucion, *Bl.*, 1890, (3), **3**, 4).

§187. Strontium. Sr = 87.63. Valence two.

1. **Properties.**—*Specific gravity*, 2.4 (Franz, *J. pr.*, 1869, **107**, 254). *Melting point*, >810°, <850° ? (*Cir. B. of S.*, 1915), and is not volatile when heated to a full red. It is a "brass-yellow" metal, malleable and ductile. It oxidizes rapidly when exposed to the air, and when heated in the air burns, as does barium, with intense illumination (Franz, *l. c.*).

2. **Occurrence.**—Strontium occurs chiefly in strontianite, $SrCO_3$, and in celestite, $SrSO_4$.

3. **Preparation.**—First isolated in 1808 by Davy by electrolysis of the hydroxide (*Trans. Royal Soc.*, 345). It is made by electrolysis of the chloride (Frey, *A.*, 1876, **183**, 367); by heating a saturated solution of $SrCl_2$ with sodium amalgam and distilling off the mercury (Franz, *l. c.*); by heating the oxide with powdered magnesium the metal is obtained mixed with **MgO** (Winkler, *B.*, 1890, **23**, 125).

4. **Oxides** and **Hydroxides.**—Strontium oxide, **SrO**, is formed by igniting the hydroxide, carbonate (greater heat required than with calcium carbonate), nitrate and all organic strontium salts. The hydroxide, $Sr(OH)_2$, is formed by the action of water on the oxide. The peroxide, $SrO_2.8H_2O$, is made by precipitating the hydroxide with H_2O_2; at 100° this loses water and becomes SrO_2, a white powder, melting at a red heat, used in bleaching works (Conroy, *J. Soc. Ind.*, 1892, **11**, 812).

5. **Solubilities.**—*a.—Metal.*—Strontium decomposes water at ordinary temperature (Winkler, *l. c.*), it is soluble in acids with evolution of hydrogen. *b.—Oxides* and *hydroxides.*—The oxide, **SrO**, is soluble in about 100 parts water at ordinary temperature, and in about five parts of boiling water forming the hydroxide (Scheibler, *Neue Zeitschrift fur Ruebenzucker*, 1881, **49**, 257). The peroxide is scarcely soluble in water or in ammonium hydroxide, soluble in acids and in ammonium chloride.

c.—*Salts.*—The chloride is slightly *deliquescent;* crystals of the nitrate and acetate effloresce. The chloride is soluble, the nitrate insoluble in absolute alcohol. The nitrate is insoluble in boiling amyl alcohol (§188, 5*c*). The *sulphate* is very sparingly soluble in water (1-10,090 at 20.1°) (Hollemann, *Z. phys. Ch.*, 1893, **12**, 131); yet sufficiently soluble to allow its use as a reagent to detect the presence of traces of barium. Less soluble in water containing ammonium salts, sodium sulphate, or sulphuric acid than in pure water; quite appreciably soluble in **HCl** or HNO_3; insoluble in alcohol. Strontium fluosilicate is soluble in water (distinction from barium). The chromate is soluble in 831.8 parts water at 15° (Fresenius, *Z.*, 1890, **29**, 419); soluble in many acids including chromic acid; and more soluble in water containing ammonium salts than in pure water.

6. **Reactions.** *a.*—The **fixed alkalis precipitate** strontium salts when not too dilute, as the hydroxide, $Sr(OH)_2$, less soluble than the barium hydroxide. No precipitate with **ammonium hydroxide.** The **alkali carbonates** precipitate solutions of strontium salts as the carbonate. Strontium sulphate is completely transposed on boiling with a fixed alkali carbonate (distinction from barium, §188, 6*a* footnote).

b.—**Oxalic acid** and **oxalates** precipitate strontium oxalate, insoluble in water, soluble in hydrochloric acid (Souchay and Lenssen, *A.*, 1857, **102**, 35). *c.*—The solubility of strontium salts is diminished by the presence of concentrated nitric acid, but less so than barium salts. *d.*—In deportment with **phosphates**, strontium is not to be distinguished from barium.

e.—See 6e, §§186 and 188. **Sulphuric acid** and **sulphates** (including $CaSO_4$) precipitate solutions of strontium salts as the sulphate, unless the solution is diluted beyond the limit of the solubility of the precipitate (5*c*). A solution of strontium sulphate is used to detect the presence of traces of barium (distinction from strontium and calcium). In dilute solutions the precipitate of strontium sulphate forms very slowly, aided by boiling or by the presence of alcohol, prevented by the presence of hydrochloric or nitric acids (5*c*). It is almost insoluble in a solution of ammonium sulphate (separation from calcium).

f.—The **halides** of strontium are all soluble in water and have no application in the analysis of strontium salts. Strong hydrochloric acid dissolves strontium sulphate, but in general diminishes the solubility of strontium salts in water. *g.*—Neutral solutions of **arsenites** do not precipitate strontium salts. The addition of ammonium hydroxide causes a precipitation of a portion of the strontium. **Arsenate** of strontium resembles the corresponding barium salt. Alkaline arsenates do not precipitate strontium from solution of the sulphate (distinction from calcium, §188, 6*g*).

h.—Normal **chromates** precipitate strontium chromate from solutions not too dilute (5*c*), soluble in acids. In absence of barium, strontium may be separated from calcium by adding to the nearly neutral solutions a solution of K_2CrO_4 plus one-third volume of alcohol. The calcium

chromate is about 100 times as soluble as the strontium chromate (Fresenius and Rubbert, *Z.*, 1891, **30**, 672). No precipitate is formed with potassium bichromate (separation from barium).

i.—**Fluosilicic** acid does not precipitate strontium salts even from quite concentrated solutions, as the strontium fluosilicate is fairly soluble in cold water and more so in the presence of hydrochloric acid (Fresenius, *Z.*, 1890, **29**, 143).

7. **Ignition.**—Volatile strontium compounds color the **flame** *crimson*. In presence of barium the crimson color appears at the moment when the substance (moistened with hydrochloric acid, if a non-volatile compound) is first brought into the flame. The paler, yellowish-red flame of calcium is liable to be mistaken for the strontium flame. The **spectrum** of strontium is characterized by eight bright bands; namely, six red, one orange and one blue. The orange line **Sr** α, at the red end of the spectrum; the two red lines, **Sr** β and **Sr** γ, and the blue line, **Sr** δ, are the most important.

8. **Detection.**—Strontium is precipitated with barium and calcium from the filtrate of the fourth group by ammonium carbonate. The well washed precipitate of the carbonates is dissolved in acetic acid and the barium removed by $K_2Cr_2O_7$. The strontium and calcium are separated from the excess of chromate by reprecipitation with $(NH_4)_2CO_3$. The precipitate is again dissolved in $HC_2H_3O_2$ and from a portion of the solution the strontium is detected by a solution of $CaSO_4$ (6*e*). The flame test (7) is of value in the identification of strontium.

9. **Estimation.**—Strontium is weighed as a sulphate or a carbonate. The hydroxide and carbonate may be determined by alkalimetry. It is separated from calcium: (*1*) By the insolubility of its sulphate in ammonium sulphate. (*2*) By boiling the nitrates with amyl alcohol (§188, 9). (*3*) By treating the nitrates with equal volume of absolute alcohol and ether (§188, 9). For separation from barium see §186, 9.

§188. Calcium. Ca = 40.07. Valence two.

1. **Properties.**—*Specific gravity*, 1.6 to 1.8 (Caron, *C. r.*, 1860, **50**, 547). *Melting point*, 810° (*Cir. B. of S.*, 1915). A white metal having very much the appearance of aluminum, is neither ductile nor malleable (Frey, *A.*, 1876, **183**, 367). In dry air it is quite stable, in moist air it burns with incandescence, as it does also with the halogens. It dissolves in mercury, forming an amalgam.

2. **Occurrence.**—Found in the mineral kingdom as a carbonate in marble, limestone, chalk and aragonite; as a sulphate in gypsum, selenite, alabaster, etc.; as a fluoride in fluor-spar; as a phosphate in apatite, phosphorite, etc. It is found as a phosphate in bones; in egg-shells and oyster-shells as a carbonate. It is found in nearly all spring and river waters.

3. **Preparation.**—(*1*) By ignition of the iodide with sodium in closed retorts (Dumas, *C. r.*, 1858, **47**, 575). (*2*) By fusion of a mixture of 300 parts fused $CaCl_2$, 400 parts granulated zinc and 100 parts **Na** until zinc vapor is given off. From the **CaZn** alloy thus obtained the zinc is removed by distillation in a graphite crucible (Caron, *l. c.*). (*3*) By electrolysis of the chloride (Frey, *l. c.*). (*4*) By reducing the oxide, hydroxide or carbonate with magnesium (Winkler, *B.*, 1890, **23**, 122 and 2642).

4. **Oxides** and **Hydroxides.**—The oxide, **CaO**, is a strong base, non-fusible, non-volatile; it is formed by oxidation of the metal in air; by ignition of the

hydroxide, the carbonate (limestone), nitrate, and all organic calcium salts. The corresponding hydroxide, $Ca(OH)_2$ (slaked lime), is made by treating the oxide with water. Its usefulness when combined with sand, making mortar, is too well known to need any description here. The peroxide, $CaO_2.8H_2O$, is made by adding hydrogen peroxide or sodium peroxide to the hydroxide: $Ca(OH)_2 + H_2O_2 = CaO_2 + 2H_2O$ (Conroy, *J. Soc. Ind.*, 1892, **11**, 808). Drying at 130° removes all the water, leaving a white powder, CaO_2, which at a red heat loses half its oxygen (Schoene, *A.*, 1877, **192**, 257). It cannot be made by heating the oxide in oxygen or with potassium chlorate (§186, 4).

5. **Solubilities.**—*a.—Metal.*—Calcium is soluble in acids with evolution of hydrogen; it decomposes water, evolving hydrogen and forming $Ca(OH)_2$.

b.—Oxide and *hydroxide.*—CaO combines with dilute acids forming corresponding salts, it absorbs CO_2 from the air becoming $CaCO_3$.* In moist air it becomes $Ca(OH)_2$, the reaction taking place rapidly and with increase of volume and generation of much heat in presence of abundance of water. The hydroxide, $Ca(OH)_2$, is soluble in acids, being capable of titration with standard acids. It is much less soluble in water than barium or strontium hydroxides (Lamy, *C. r.*, 1878, **86**, 333); in 806 parts at 19.5° (Paresi and Rotondi, *B.*, 1874, **7**, 817); and in 1712 parts at 100° (Lamy, *l. c.*). The solubility decreases with increase of temperature. In saturated solutions one part of the oxide is found in 744 parts of water at 15° (Lamy, *l. c.*). A clear solution of the hydroxide in water is lime water (absorbs CO_2 forming $CaCO_3$), the hydroxide in suspension to a greater or less creamy consistency is milk of lime.

c.—Salts.—The chloride, bromide, iodide, nitrate, and chlorate are *deliquescent;* the acetate is efflorescent.

The carbonate, oxalate, and phosphate are insoluble in water. The chloride, iodide, and nitrate are soluble in alcohol. The nitrate is soluble in 1.87 parts of equal volumes of ether and alcohol (Fresenius, *Z.*, 1893, **32**, 191); readily soluble in boiling amyl alcohol (Browning, *Am. S.*, 1892, **143**, 53 and 314) (separation from barium and strontium). The carbonate is soluble in water saturated with carbonic acid (as also are barium, strontium, and magnesium carbonates), giving hardness to water. The oxalate is insoluble in acetic acid, soluble in hydrochloric and nitric acids. The *sulphate* is soluble in about 500 parts of water † at ordinary temperature, the solubility not varying much in hot water until above 100° when the solubility rapidly decreases. Its solubility in most alkali salts is greater than in pure water. Ammonium sulphate (1-4) requires 287 parts for the solution of one part of $CaSO_4$ (Fresenius, *Z.*, 1891, **30**, 593) (separation from **Ba** and **Sr**). Readily soluble in a solution of $Na_2S_2O_3$ (separation from barium sulphate) (Diehl, *J. pr.*, 1860, **79**, 430). It is soluble in 60 parts hydrochloric acid, 6.12 per cent at 25°, and in 21 parts of the same

* Dry CaO does not absorb dry CO_2 or SO_2 below 350°. (Veley, *J. C.*, 1893, **63**, 821).

† Goldhammer, *C. C.*, 1888, 708; Drocze, *B.*, 1877, **10**, 330; Boisbaudran, *A. Ch.*, 1874. (5), **3**, 477 Kohlrausch and Rose, *Z. phys. Ch.*, 1893, **12**, 241; Raupenstrauch, *M.*, 1885, **6**, 563).

acid at 103° (Lunge, *J. Soc. Ind.*, 1895 **14**, 31). The chromate is soluble in 214.3 parts water at 14° (Siewert, *J.*, 1862, 149); in dilute alcohol it is rather more soluble (Fresenius, *l. c.*, page 672); very readily soluble in acids including chromic acid.

6. **Reactions.** *a.*—The **fixed alkali hydroxides** precipitate solutions of calcium salts not having a degree of dilution beyond the solubility of the calcium hydroxide formed (*5b*), *i. e.* potassium hydroxide will form a precipitate with calcium sulphate since the sulphate requires less water for its solution than the hydroxide (*5b* and *c*); also the calcium hydroxide is less soluble in the alkaline solution than in pure water. **Ammonium hydroxide** does not precipitate calcium salts. The **alkali carbonates** precipitate calcium carbonate, $CaCO_3$, insoluble in water free from carbon dioxide, decomposed by acids. Calcium sulphate is completely transposed upon digestion with an alkali carbonate * (distinction from barium). Calcium hydroxide, $Ca(OH)_2$, is used as a reagent for the detection of carbon dioxide (*5b* and §**228**, 8).

b.—Alkali **oxalates**, as $(NH_4)_2C_2O_4$, precipitate *calcium oxalate*, CaC_2O_4, from even dilute solutions of calcium salts. The precipitate is scarcely at all soluble in *acetic* or oxalic acids (separation of oxalic from phosphoric acid (§**315**), but is soluble in *hydrochloric* and nitric acids. The precipitation is hastened by presence of ammonium hydroxide. Formed slowly, from very dilute solutions, the precipitate is crystalline, octahedral. If **Sr** or **Ba** are possibly present in the solution to be tested (qualitatively), an alkali *sulphate* must first be added, and *after digesting a few minutes*, if a precipitate appears, $SrSO_4$, $BaSO_4$, or, if the solution was concentrated, perhaps $CaSO_4$, it is filtered out, and the oxalate then added to the filtrate. If a mixture of the salts of barium, strontium, and calcium in neutral or alkaline solution be treated with a mixture of $(NH_4)_2SO_4$ and $(NH_4)_2C_2O_4$, the barium and strontium are precipitated as sulphates and the calcium as the oxalate; separated from the barium and strontium on addition of hydrochloric acid (Sidersky, *Z.*, 1883, **22**, 10; Bozomoletz, *B.*, 1884, **17**, 1058). A solution of calcium chloride is used as a reagent for the detection of oxalic acid (§**227**, 8).

In solutions of calcium salts containing a strong excess of ammonium chloride, potassium ferrocyanide precipitates the calcium (distinction from barium and strontium) (Baubigny, *Bl.*, 1895, (3), **13**, 326).

* Here experiment shows that for equilibrium the SO_4 ions must be present in solution in large excess of CO_3 ions. With strontium also an excess of SO_4 ions is required, although not so great as in the case of calcium. For barium, however, equilibrium demands that the concentration of CO_3 ions exceed that of SO_4. This condition is already fulfilled when an alkali carbonate is added to $BaSO_4$ and therefore no change takes place in this case, while in the others the sulphate is transformed into carbonate. It is important to notice that the relative or absolute quantities of solid carbonate and sulphate present do not affect the equilibrium, which is determined solely by the substances in solution (§**57**, 6*e*, footnote).

c.—See 5*c*. *d.*—By the action of alkali phosphates, solutions of calcium are not distinguished from solutions of barium or strontium.

e.—Pure sodium sulphide, Na_2S, gives an abundant precipitate with calcium salts; even with $CaSO_4$. The precipitate is $Ca(OH)_2$: $CaCl_2 + 2Na_2S + 2H_2O = Ca(OH)_2 + 2NaCl + 2NaHS$. The acid sulphide, $NaHS$, does not precipitate calcium salts (Pelouze, *A. Ch.*, 1866, (4), **7**, 172). Alkali **sulphites** precipitate calcium sulphite, nearly insoluble in water, soluble in hydrochloric, nitric or sulphurous acid; barium and strontium salts act similarly.

Sulphuric acid and soluble **sulphates** precipitate calcium salts as $CaSO_4$, distinguished from barium by its solubility in water and in hydrochloric acid; from barium and strontium by its solubility in ammonium sulphate (5*c*). A water solution of calcium sulphate is used to detect strontium after barium has been removed as a chromate. Obviously a solution of strontium sulphate will not precipitate calcium salts.

f.—Calcium **chloride**, fused, is much used as a drying agent for solids, liquids and gases. **Chlorinated lime**, or bleaching powder, $CaCl_2O$ (Kingzett, *J. C.*, 1875, **28**, 404), is much used as a bleaching agent and as a disinfectant. *g.*—Neutral or ammoniacal solutions of **arsenites** form a precipitate with calcium salts (distinction from barium). A solution of calcium salts including solutions of calcium sulphate in ammoniacal solution is precipitated by **arsenic acid** as $CaNH_4AsO_4$ (distinction from strontium after the addition of sulphuric acid) (Bloxam, *C. N.*, 1886, **54**, 16).

h.—Normal **chromates**, as K_2CrO_4, precipitate solutions of calcium salts as calcium chromate, $CaCrO_4$, yellow, provided the solution be not too dilute (5*c*). The precipitate is readily soluble in acids and is not formed with acid chromates as $K_2Cr_2O_7$ (separation from barium). *i.*—**Fluosilicic** acid does not precipitate calcium salts even in the presence of equal parts of alcohol (separation from barium).

7. **Ignition.**—Calcium sulphate, $CaSO_4.2H_2O$, gypsum, loses its water of crystallization at 80° and becomes the anhydrous sulphate, $CaSO_4$, plaster of Paris; which on being moistened forms the crystalline $CaSO_4.2H_2O$, expands and "sets." Calcium carbonate, *limestone*, when heated (burned) loses carbon dioxide and becomes lime, CaO.

Compounds of calcium, preferably the chloride, render the **flame** *yellowish red*. The presence of strontium or barium obscures this reaction, but a mixture containing calcium and barium, moistened with hydrochloric acid, gives the calcium color on its first introduction to the flame. The **spectrum** of calcium is distinguished by the bright green line, **Ca** β, and the intensely bright orange line, **Ca** α, near the red end of the spectrum.

8. **Detection.**—Calcium is separated in analysis from the metals of the other groups and from barium, with strontium, as described at §**187**, 8. A portion of the solution of strontium and calcium acetate is boiled with potassium sulphate; after standing for some time (ten minutes), the filtrate is tested with ammonium oxalate. A white precipitate insoluble in the acetic acid present, but soluble in hydrochloric acid is evidence of the presence of calcium. The flame test (7) is confirmatory.

9. **Estimation.**—Calcium is weighed as an oxide, carbonate, or sulphate. The carbonate is obtained by precipitating as oxalate, and gently igniting the dried precipitate; higher ignition changes the carbonate to the oxide. The sulphate is precipitated in a mixture of two parts of alcohol to one of the solution. The hydroxide and carbonate may be determined by alkalimetry. Calcium may be separated from barium and strontium by the solution of its nitrate in amyl

alcohol (5*c*). The best method of separation from strontium is to treat the nitrates with a mixture of equal volumes of alcohol and ether. The calcium nitrate dissolves, but not more than one part in 60,000 of the strontium is found in the solution (§195). In the presence of iron, aluminum and phosphoric acid, calcium is best precipitated as an oxalate in the presence of citric acid (Passon, *Z. angew.*, 1898, 776). See also 9, §186 and §187.

§189. Magnesium. $Mg = 24.32$. Valence two.

1. **Properties.**—*Specific gravity*, 1.75 (Deville and Caron, *A. Ch.*, 1863, (3), **67**, 346); *melting point*, 651° (*Cir. B. of S.*, 1915). A white, hard, malleable and ductile metal; not acted upon by water or alkalis at ordinary temperature and only slightly at 100° (Ballo, *B.*, 1883, **16**, 694). When heated in air or in oxygen it burns with incandescence to **MgO**. It combines directly when heated in contact with **N**, **P**, **As**, **S** and **Cl**. It forms alloys with **Hg** and **Sn**, forming compounds which decompose water.

2. **Occurrence.**—Magnesite, $MgCO_3$; dolomite, $CaMg(CO_3)_2$; brucite, $Mg(OH)_2$; epsom salts, $MgSO_4.7H_2O$; and combined with other metals in a great variety of minerals.

3. **Preparation.**—(*1*) By electrolysis of the chloride or sulphate (Bunsen, *A.*, 1852, **82**, 137). (*2*) By ignition of the chloride with sodium or potassium (Wöhler, *A.*, 1857, **101**, 562). (*3*) $Mg_2Fe(CN)_6$ is ignited with Na_2CO_3, and this product ignited with zinc (Lanterbronn, German Patent No. 39,915).

4. **Oxide** and **Hydroxide.**—Only one oxide of magnesium, **MgO**, is known with certainty. Formed by burning the metal in the air, and by action of heat upon the hydroxide, carbonate, nitrate, sulphate, oxalate and other magnesium salts decomposed by heat. The corresponding hydroxide, $Mg(OH)_2$, is formed by precipitating magnesium salts with the fixed alkalis.

5. **Solubilities.**—*a.*—*Metal.*—Magnesium is soluble in acids including carbonic acid, evolving hydrogen: $Mg + CO_2 + H_2O = MgCO_3 + H_2$ (Ballo, *B.*, 1882, **15**, 3003): it is also attacked by the acid alkali carbonates, as $NaHCO_3$, to form $MgCO_3$, Na_2CO_3 and **H** (Ballo, *l. c.*). Soluble in ammonium salts: $Mg + 3NH_4Cl = NH_4MgCl_3 + 2NH_3 + H_2$. With the halogens it acts tardily (Wanklyn and Chapman, *J. C.*, 1866, **19**, 141). *b.*—*Oxide* and *hydroxide.*—Insoluble in water, soluble in acids. $Mg(OH)_2$ is soluble in 111,111 parts of water at 18° (Kohlrausch and Rose, *Zeit. phys. Ch.*, 1893, **12**, 241). In contact with water the oxide is slowly changed to the hydroxide, $Mg(OH)_2$, and absorbs CO_2 from the air. Soluble in ammonium salts:* $Mg(OH)_2 + 3NH_4Cl = NH_4MgCl_3 + 2NH_4OH$. *c.*—*Salts.*—The chloride, bromide, iodide, chlorate, nitrate, and acetate (4 aq) are *deliquescent*; the sulphate (7 aq) slightly efflorescent. The carbonate, phosphate, borate, arsenite, and arsenate are insoluble in water; the sulphite, oxalate, and chromate soluble; the tartrate sparingly soluble. The carbonate is soluble; the phosphate, arsenite, and arsenate are insoluble in excess of ammonium salts.

6. **Reactions.** *a.*—The **fixed alkali hydroxides** and the **hydroxides** of **barium, strontium** and **calcium** precipitate magnesium hydroxide, $Mg(OH)_2$,

* The conditions here are the same as in the case of $Mn(OH)_2$, §134, 6*a*, footnote.

white, gelatinous, from solutions of magnesium salts; insoluble in excess of the reagent but readily soluble in ammonium salts, the magnesium passing into the negative ion: $\overset{++}{Mg}(OH)_2 + 4\overset{+}{N}H_4\overset{-}{Cl} = (NH_4)_2\overset{++}{Mg}\overset{--}{Cl_4} + 2NH_4OH$. With **ammonium hydroxide** but half of the magnesium is precipitated, the remainder being held in solution in the acid ion by the ammonium salt formed in the reaction: $2\overset{++}{Mg}\ \overset{--}{SO_4} + 2\overset{+}{N}H_4\overset{-}{O}H = \overset{++}{Mg}(OH)_2 + (\overset{+}{N}H_4)_2\overset{--}{Mg}(\overset{--}{SO_4})_2$ (Rheineck, *Dingl.*, 1871, **202**, 268). The **fixed alkali** carbonates precipitate basic magnesium carbonate, $Mg_4(OH)_2(CO_3)_3$, variable to $Mg_5(OH)_2(CO_3)_4$: $4MgSO_4 + 4Na_2CO_3 + H_2O = Mg_4(OH)_2(CO_3)_3 + Na_2SO_4 + CO_2$. If the above reaction takes place in the cold the carbon dioxide combines with a portion of the magnesium carbonate to form a soluble acid magnesium carbonate: $5MgSO_4 + 5Na_2CO_3 + 2H_2O = Mg_4(OH)_2(CO_3)_3 + MgH_2(CO_3)_2 + 5Na_2SO_4$. On boiling, the acid carbonate is decomposed with escape of CO_2. **Ammonium carbonate** does not precipitate magnesium salts, as a soluble double salt is at once formed. **Acid fixed alkali carbonates**, as $NaHCO_3$, do not precipitate magnesium salts in the cold; but upon boiling, CO_2 is evolved and the carbonate is precipitated (Engel, *A. Ch.*, 1886, (6), **7**, 260).

b.—Soluble **oxalates** do not precipitate solutions of magnesium salts, as they form soluble double oxalates. If to the solution of double oxalates, preferably magnesium ammonium oxalate, an equal volume of 80 per cent acetic acid be added, the magnesium is precipitated as the oxalate (separation from potassium or sodium (Classen, *Z.*, 1879, **18**, 373).

d.—Alkali **phosphates**—as Na_2HPO_4—precipitate *magnesium phosphate*, $MgHPO_4$, if the solution be not very dilute. But even in very dilute solutions, by the further addition of ammonium hydroxide (and NH_4Cl), a crystalline precipitate is slowly formed, *magnesium ammonium phosphate* —$MgNH_4PO_4$. Stirring with a glass rod against the side of the test-tube promotes the precipitation. The addition of ammonium chloride, in this test, prevents formation of any precipitate of magnesium hydroxide (5*b*). The precipitate dissolves in 13,497 parts of water at 23° (Ebermayer, *J. pr.*, 1853, **60**, 41); almost absolutely insoluble in water containing ammonium hydroxide and ammonium chloride (Kubel, *Z.*, 1869, **8**, 125).

e.—Magnesium *sulphide* is decomposed by water, and magnesium salts are not precipitated by **hydrosulphuric acid** or **ammonium sulphide**; but $MgO + H_2O$ (1-10) absorbs H_2S, forming in solution MgH_2S_2, which readily gives off H_2S upon boiling (a very satisfactory method of preparing H_2S absolutely arsenic free) (Divers and Shmidzu, *J. C.*, 1884, **45**, 699). Normal sodium or potassium sulphide precipitates solutions of magnesium salts as the hydroxide with formation of an acid alkali sulphide: $MgSO_4 + 2Na_2S + 2H_2O = Mg(OH)_2 + Na_2SO_4 + 2NaHS$ (Pelouze, *A. Ch.*, 1866, (4), **7**, 172). **Sulphuric acid** and soluble **sulphates** do not precipitate solutions of magnesium salts (distinction from **Ba**, **Sr** and **Ca**).

f.—Magnesium chloride, in solution, evaporated on the water bath evolves

hydrochloric acid (7). *g*.—Soluble **arsenates** precipitate magnesium salts in deportment similar to the corresponding phosphates.

7. **Ignition.**—Magnesium ammonium phosphate when ignited loses ammonia and water, and becomes the pyrophosphate: $2MgNH_4PO_4 = Mg_2P_2O_7 + H_2O + 2NH_3$. The carbonate loses CO_2 and becomes **MgO**. In dry air magnesium chloride may be ignited without decomposition, but in the presence of steam **MgO** and **HCl** are formed: $MgCl_2 + H_2O = MgO + 2HCl$; a technical method for preparing **HCl** (Heumann, *A.*, 1877, **184**, 227).

8. **Detection.**—If sufficient ammonium salts have been used, the magnesium will be in the filtrate from the precipitated carbonates of barium, strontium and calcium. From a portion of this filtrate the magnesium is precipitated as the white magnesium ammonium-phosphate, $MgNH_4PO_4$, by Na_2HPO_4.

9. **Estimation.**—After removal of other non-alkali metals, magnesium is precipitated as $MgNH_4PO_4$, then changed by ignition to $Mg_2P_2O_7$ (magnesium pyrophosphate) and weighed as such. Separated as $MgCl_2$ from **KCl** and **NaCl** by solution in amyl alcohol, evaporated with H_2SO_4 and weighed as $MgSO_4$ (Riggs, *Am. S.*, 1892, **44**, 103). It is estimated volumetrically by precipitation as $MgNH_4PO_4$, drying at about 50° until all free NH_4OH is removed. An excess of standard acid is then added and at once titrated back with standard fixed alkali, using methyl orange as an indicator (Handy, *J. Am. Soc.*, 1900, **22**, 31).

10. **Oxidation.**—Magnesium is a powerful reducer; ignited with the oxides or carbonates of the following elements magnesium oxide is formed and the corresponding element is liberated: **Ag**, **Hg**, **Pt**, **Sn** *, **B**, **Al**, **Th**, **C** ‡, **Si**, **Pb**, **P** ‡, **As**, **Sb**, **Bi**, **Cr**, **Mo**, **Mn**, **Fe**, **Co**, **Ni**, **Cu**, **Cd**, **Zn**, **Gl**, **Ba**, **Sr**, **Ca**, **Rb**, **K**, **Na**, and **Li**. In some cases the reaction takes place with explosive violence. From their corresponding salts in neutral solution **Mg** precipitates **Se**, **Te**, **As**, **Sb**, **Bi**, **Sn**, **Zn** †, **Cd**, **Pb**, **Tl**, **Th**, **Cu**, **Ag**, **Mn** †, **Fe** †, **Co**, **Ni**, **Au**, **Pt**, and **Pd** (Scheibler, *B.*, 1870, **3**, 295; Villiers and Borg, *C. r.*, 1893, **116**, 1524).

* Winkler, *B.*, 1890, **23**, 44, 120 and 772; 1891, **24**, 898.
† Kern, *C. N.*, 1876, **33**, 112 and 236.
‡ Seubert and Schmidt, *A.*, 1892, **267**, 218.

§190. Table for Analysis of the Fifth Group (Calcium Group).

(The Method of Separation given in §195 may be used instead of this.)
(Concerning the loss of traces of barium and calcium, see §192, *2*.)

To the filtrate from the fourth group (§138) add ammonium hydroxide and carbonate, warm but do not boil (§192, *2*). Filter and wash.

Precipitate: $BaCO_3$, $SrCO_3$, $CaCO_3$.

Dissolve the well-washed precipitate in dilute acetic acid.

Solution: $Ba(C_2H_3O_2)_2$, $Sr(C_2H_3O_2)_2$, $Ca(C_2H_3O_2)_2$.

To a small portion of the solution, add potassium dichromate; if a precipitate appears, add the reagent to the whole solution as long as a precipitate is produced (§186, 6*h*) and filter.

Precipitate: $BaCrO_4$, yellow.

The precipitate is soluble in hydrochloric acid, and this solution is precipitated by sulphuric acid, as $BaSO_4$, insoluble in acids.

Test the above hydrochloric acid solution with a loop of platinum wire in the flame. Barium gives a green flame (§186, 7).

Study §175 and *ff*., §186, §191 and §192.

Solution: $Sr(C_2H_3O_2)_2$, $Ca(C_2H_3O_2)_2$, $(K_2Cr_2O_7)$.

Reprecipitate (§192, *4* and *5*) with ammonium hydroxide and carbonate; filter, wash the precipitate, and dissolve it by acetic acid.

Solution: $Sr(C_2H_3O_2)_2$, $Ca(C_2H_3O_2)_2$.

Divide into two portions.

For Strontium:

To a portion, add solution of calcium sulphate; boil and leave for about ten minutes. A precipitate indicates strontium, $SrSO_4$ (§187, 6*e*).

Moisten the precipitate with HCl and test the solution on a loop of platinum wire, by the flame (§187, 7). Crimson flame indicates strontium.

Study §175 and *ff*., §187, §191 and §192.

For Calcium:

Add solution of ammonium sulphate (1–4), boil, allow to stand ten minutes and filter to insure the absence of strontium (§187, 5*c*).

To the filtrate (or solution not precipitated), add ammonium oxalate.

A precipitate (CaC_2O_4), white, insoluble in acetic acid, soluble in hydrochloric, indicates calcium.

Test by the flame (§188, 7).

Study §175 and *ff*., §188, §191 and §192.

Solution: Salts of Magnesium (§194, *1*) and the Alkali Metals.

To the solution in which $(NH_4)_2CO_3$ fails to give a precipitate, add a drop or two of $(NH_4)_2SO_4$ and then a few drops of $(NH_4)_2C_2O_4$ (§194, *2*). If a precipitate is obtained (showing presence of traces of **Ba**, or **Ca**), filter; and to a portion of the clear filtrate add Na_2HPO_4. A white precipitate, $MgNH_4PO_4$, indicates magnesium.

The other portion of this clear filtrate is to be tested for the presence of the alkali metals (§211).

Directions for Analysis of the Metals of the Calcium Group.

(The Alkaline Earths.)

§191. Manipulation.—To the filtrate from the fourth group in which H_2S (§192, *1*) gives no precipitate (§138) add NH_4OH and ammonium carbonate as long as a precipitate is formed: $BaCl_2 + (NH_4)_2CO_3 = BaCO_3 + 2NH_4Cl$. Digest with warming, filter and wash. The filtrate should be tested again with ammonium carbonate and if no precipitate is formed it is set aside to be tested for magnesium and the alkali metals (§§193 and 211).

The well washed white precipitate is dissolved in acetic acid, using as little as possible: $SrCO_3 + 2HC_2H_3O_2 = Sr(C_2H_3O_2)_2 + CO_2 + H_2O$.

To a small portion of the acetic acid solution add a drop of $K_2Cr_2O_7$; if a precipitate—$BaCrO_4$—is obtained, the $K_2Cr_2O_7$ must be added to the whole solution: $2Ba(C_2H_3O_2)_2 + K_2Cr_2O_7 + H_2O = 2BaCrO_4 + 2KC_2H_3O_2 + 2HC_2H_3O_2$. Filter, wash the precipitate and dissolve it in **HCl**. Test a portion in the flame and precipitate the barium in the remainder as barium sulphate, with a drop of sulphuric acid.

To the filtrate from the barium chromate add NH_4OH and $(NH_4)_2CO_3$, warm, filter, and wash. Dissolve the white precipitates of $SrCO_3$ and $CaCO_3$ in acetic acid and divide the solution into two portions.

Portion 1.—For *Strontium.*—With a platinum wire obtain the flame test, crimson for strontium; calcium interferes (?, §§187, 188 and 205). Add a solution of **calcium sulphate** and boil; set aside for about ten minutes. A precipitate—$SrSO_4$—indicates strontium. This $SrSO_4$ may be moistened with **HCl** and the crimson flame test obtained.

Portion 2.—For *Calcium.*—Add a solution of **ammonium** (1–4) **sulphate,** boil, and set aside for ten minutes. Filter (to remove any strontium that may be present; also a portion of the calcium may be precipitated, §188, 6*c*.) and add **ammonium oxalate** to the filtrate. Dissolve the precipitate in **HCl**. A white precipitate—CaC_2O_4—insoluble in acetic acid by its formation in that solution, and soluble in **HCl** is proof of the presence of calcium.

§192. *Notes.—1.* Considerable amounts of the metals of this group, especially barium and strontium, may be precipitated with the second group on account of the formation of sulphuric acid by the oxidation of hydrogen sulphide, especially by means of ferric chloride. As much as 15 mg. of barium may be precipitated in this manner. A still further loss of 15 mg. of barium as well as considerable quantities of calcium and strontium as carbonates may occur during the precipitation of the iron group. Smaller quantities may be precipitated as sulphate or carbonate with the ammonium sulphide group. (Curtman and Frankel, *J. Am. Soc.*, **33**, 724 (1911).)

If large quantities of the metals in the preceding groups; especially iron, are present, barium, strontium and calcium may fail to be detected for this reason, by the ammonium carbonate method of separation. The method of Curtman and Frankel should then be used. See §197.

2. Do not boil after the addition of ammonium carbonate, as this will drive off

ammonium hydroxide and carbonate, increasing the solubility of the $CaCO_3$ (note 3 and §178).

3. The **precipitation of barium, strontium** and **calcium** by ammonium carbonate in the presence of ammonium chloride is not as complete as would be desirable in very delicate analyses. The carbonates of barium, strontium and calcium are all slightly soluble in ammonium chloride solution; and while the prescribed addition of ammonium hydroxide, and excess of ammonium carbonate, greatly reduces the solubility of the precipitated carbonates, yet even with these the precipitation is not absolute, though more nearly so with strontium than with barium and calcium. Thus, in *quantitative* analyses, if barium and calcium are precipitated as carbonates, it must be done in the absence of ammonium chloride or sulphate, and the precipitate washed with water containing ammonium hydroxide. As much as 10 mg. of barium may remain in solution in the presence of much ammonium salts. (Curtman and Frankel, *J. Am. Soc.*, **33**, 724 (1911).)

4. If barium be absent, as evidenced by the failure to obtain a precipitate with $K_2Cr_2O_7$, the solution may at once be divided into two portions to test for strontium and calcium.

5. With care the reprecipitation by ammonium carbonate, for the separation from the excess of $K_2Cr_2O_7$, may be neglected and the filtrate from the barium, yellow, at once divided into two portions and tested for **Sr** and **Ca**. Reprecipitation always causes the loss of some of the metals, due to the solubility of the carbonates in the ammonium acetate formed. On the other hand, traces may escape observation in the yellow chromate solution.

6. Before reprecipitation with $(NH_4)_2CO_3$, an excess of ammonium hydroxide should be added to prevent the liberation of CO_2 when the ammonium carbonate is added.

7. Strontium sulphate is so sparingly soluble in water (§187, 5*c*) that its precipitation by $CaSO_4$ (or other sulphates in absence of **Ca**) is sufficiently delicate to detect very small amounts of that metal. However, it is sufficiently soluble in water to serve as a valuable reagent to detect the presence of traces of barium. Obviously $SrSO_4$ will not precipitate solutions of calcium salts. Solutions of strontium and barium salts (except $SrSO_4$) are all precipitated by $CaSO_4$. The presence of excess of calcium salts lessens the delicacy of the precipitation of strontium salts by calcium sulphate.

8.—In very dilute solutions the sulphates of the alkaline earths are not precipitated rapidly. Time should be allowed for the complete precipitation. Boiling and evaporation facilitates the reaction.

9. It should be noticed that the test for calcium as an oxalate is made upon that portion of the calcium not removed by $(NH_4)_2SO_4$; or in other words upon a solution of $CaSO_4$ (1–287). A solution of $SrSO_4$ (1–10,000) may be present, but is not precipitated by $(NH_4)_2C_2O_4$. The presence of a great excess of $(NH_4)_2SO_4$ prevents the precipitation of traces of calcium salts by $(NH_4)_2C_2O_4$.

§193. **Manipulation.**—To a portion of the filtrate from the carbonates of **Ba**, **Sr**, and **Ca** add a drop or two of $(NH_4)_2SO_4$. A slight precipitate indicates a trace of barium. To the filtrate a few drops of $(NH_4)_2C_2O_4$ are added. A trace of calcium is indicated by a slight precipitate. Filter if a precipitate is obtained and test the filtrate for **Mg** with Na_2HPO_4. A white crystalline precipitate—$MgNH_4PO_4$—is evidence of the presence of magnesium. The other portion of the filtrate from the carbonates of **Ba**, **Sr**, and **Ca** is reserved to be tested for the alkali metals (§211).

§194. *Notes.—1.* By some, magnesium is classed in the last or alkali group instead of in the alkaline earth group. It is not precipitated by the $(NH_4)_2CO_3$, yet in the general properties of its salts it is so closely related to **Ba**, **Sr** and **Ca**, that it is much better regarded as a subdivision of that group than as belonging to the alkali group (§175 and *ff.*).

2. Traces of **Ba**, **Sr** and **Ca** may remain in solution after adding $(NH_4)_2CO_3$ and warming; due to the solvent action of the ammonium salts present. To pre-

vent these traces giving a test for magnesium with Na_2HPO_4 a drop or two of $(NH_4)_2SO_4$ is added to remove barium or strontium and a few drops of $(NH_4)_2C_2O_4$ to remove calcium. The precipitate (if any forms) is removed by filtration, before the Na_2HPO_4 is added.

3. The precipitate of $MgNH_4PO_4$ does not always form rapidly, if only small amounts of **Mg** are present, and the solution should be allowed to stand. Rubbing the sides of the test tube with a glass stirring rod promotes the precipitation.

4. The precipitation of **Mg** as $MgNH_4PO_4$ is fairly delicate (1-71,492) (Kissel, *Z.*, 1869, **8**, 173); but *not very characteristic*, as the phosphates of nearly all the metals are white and insoluble in water. Hence the reliability of this test for magnesium depends upon the *rigid exclusion* of the other metals (not alkalis) by the previous processes of analysis. The precipitate should be carefully examined with a magnifying glass to ascertain if it is crystalline which is characteristic of magnesium ammonium phosphate. Small amounts of aluminum may be present at this point and a small amorphous precipitate may be aluminum phosphate. It should be filtered off and treated with a few drops of acetic acid which readily dissolves magnesium ammonium phosphate, but not aluminum phosphate. The filtrate should be neutralized with ammonia and a few drops of Na_2HPO_4 added. On standing for some time small transparent crystals are deposited on the walls of the test tube if magnesium is present.

5. Lithium phosphate is not readily soluble in water or ammonium salts and may give a test for magnesium. See §210, 6*d*.

§195. The unlike solubilities in **alcohol**, of the **chlorides** and **nitrates** of barium, strontium and calcium enable us to separate them very closely by absolute alcohol, and approximately by "strong alcohol," as follows:

Dissolve the carbonate precipitate in **HCl**, evaporate to dryness on the water-bath, rub the residue to a fine powder in the evaporating dish, and digest it with alcohol. Filter through a small filter, and wash with alcohol (5*c*, §§186, 187 and 188).

Residue: $BaCl_2$.	**Filtrate: $SrCl_2$ and $CaCl_2$.**	
Dissolve in water, test with $CaSO_4$, $SrSO_4$, $K_2Cr_2O_7$, etc.	Evaporate to dryness, change to nitrates by adding a few drops of HNO_3. Evaporate the nitrates to dryness, powder, digest with alcohol,* filter and wash with alcohol (or digest and wash with equal volumes of alcohol and ether.)	
	Residue: $Sr(NO_3)_2$.	**Filtrate: $Ca(NO_3)_2$.**
	Precipitation by $CaSO_4$ in water solution: flame test, etc.	Precipitation by H_2SO_4 in alcohol solution, by $(NH_4)_2C_2O_4$, etc.

Or, the alcoholic filtrate of $SrCl_2$ and $CaCl_2$ may be precipitated with (a drop of) sulphuric acid, the precipitate filtered out and digested with solution of $(NH_4)_2SO_4$ and a little NH_4OH. *Residue*, $SrSO_4$. *Solution* contains $CaSO_4$, precipitable by oxalates.

§196. If the alkaline earth metals are present in the original material as **phosphates**, or in mixtures such that the treatment for solution will bring them in contact with phosphoric acid; the process of analysis must be modified. One of the methods given under analysis of third and fourth group metals in presence of phosphates (§145 and *ff.*) must be employed.

§197. The presence of **oxalates** will also interfere, necessitating the evaporation and ignition to decompose the oxalic acid (§151).

*Instead of alcohol the residue of the nitrates may be boiled with amyl alcohol. Calcium nitrate is dissolved making a complete separation from the strontium nitrate (§188, 5*c*).

THE ALKALI GROUP (SIXTH GROUP).

Potassium. $K = 39.10$. **Caesium.** $Cs = 132.81$.

Sodium. $Na = 23.00$. **Rubidium.** $Rb = 85.45$.

Ammonium. $(NH_4)'$. **Lithium.** $Li = 6.94$.

§198. The metals of the alkalis are highly combustible, oxidizing quickly in the air, displacing the hydrogen of water even more rapidly than zinc or iron displaces the hydrogen of acids, and displacing non-alkali metals from their oxides and salts. As elements they are very strong reducing agents, while their compounds are very stable, and not liable to either reduction or oxidation by ordinary means. The five metals, **Cs**, **Rb**, **K**, **Na**, **Li**, present a gradation of electro-positive or basic power, cæsium being strongest, and the others decreasing in the order of their atomic weights, lithium decomposing water with less violence than the others. Their specific gravities decrease,* their fusing points rise, and as carbonates their solubilities lessen, in the same order. In solubility of the phosphate, also, lithium approaches the character of an alkaline earth (§6).

Ammonium is the basal radical of ammonium salts, and as such has many of the characteristics of an alkali metal. The water solution of the gas ammonia, NH_3 (an anhydride), from analogy is supposed to contain ammonium hydroxide, NH_4OH, known as *the volatile alkali*. Potassium and sodium hydroxides are *the fixed alkalis* in common use.

§199. The alkalis are very **soluble** in water, and *all the important salts of the alkali metals* (including NH_4) *are soluble* in water, not excepting their carbonates, phosphates (except lithium), and silicates; while *all other* metals form hydroxides or oxides, either insoluble or sparingly soluble, and carbonates, phosphates, silicates, and certain other salts quite insoluble in water.

Their compounds being nearly all soluble, the alkali metals are *not precipitated* by ordinary reagents, and, with few exceptions, their salts do not precipitate each other. **In analysis**, they are mostly separated from other metals by non-precipitation.

§200. In accordance with the insolubility in water of the non-alkali hydroxides and oxides, *the alkali hydroxides precipitate all non-alkali metals*, except that ammonium hydroxide does not precipitate barium, strontium, and calcium. These precipitates are hydroxides, except those of mercury, silver, and antimony. But certain of the non-alkali hydroxides and oxides, though insoluble in water, dissolve in solutions of alkalis; hence, when added in excess, *the alkalis redissolve the precipitates they at first produce with salts of certain metals*, viz.: the hydroxides of **Pb**, **Sn**, **Sb** (oxide),

* Except those of potassium (0.875) and sodium (0.9735).

Zn, **Al**, and **Cr** dissolve in the fixed alkalis; and oxide of **Ag** and hydroxides of **Cu**, **Cd**, **Zn**, **Co**, and **Ni** dissolve in the volatile alkali.

§**201.** Solutions of the alkalis are caustic to the taste and touch, and turn red **litmus** blue; also, the carbonates, acid carbonates, normal and dibasic phosphates, and some other salts of the alkali metals, give the "alkaline reaction" with test papers. **Sodium nitroferricyanide**, with hydrogen sulphide, gives a delicate reaction for the alkali hydroxides (§**207**, 6*b*).

§**202.** The hydroxides and normal carbonates of the alkali metals are not decomposed by **heat** alone (as are those of other metals), and these metals form the only acid carbonates obtained in the solid state.

§**203.** The fixed alkalis, likewise many of their salts, melt on **platinum foil** in the flame, and slowly vaporize at a bright red heat. All salts of ammonium, by a careful evaporation of their solutions on platinum foil, may be obtained in a solid residue, which rapidly vaporizes, wholly or partly, below a red heat (distinction from fixed alkali metals).

§**204.** The hydroxides of the fixed alkali metals, and those of their salts most volatile at a red heat, preferably their chlorides, impart strongly characteristic colors to a non-luminous **flame**, and give well-defined **spectra** with the spectroscope.

§205. Potassium. K = 39.10. Valence one.

1. **Properties**—*Specific gravity*, 0.875 at 13° (Baumhauer, *B.*, 1873, **6**, 655). *Melting point*, 62.3° (*Cir. B. of S.*, 1915). *Boiling point*, 719° to 731° (Carnelley and Williams, *B.*, 1879, **12**, 1360); 667° (Perman, *J. C.*, 1889, **55**, 328). Silver-white metal with a bluish tinge. At ordinary temperature of a wax-like consistency, ductile and malleable; at 0° it is brittle. It is harder than **Na** and is scratched by **Li**, **Pb**, **Ca** and **Sr**. The glowing vapor is a very beautiful intense violet (Dudley, *Am.*, 1892, **14**, 185). It is next to caesium and rubidium, the most electro-positive of all metals, remains unchanged in dry air, oxidizes rapidly in moist air, and decomposes water with great violence, evolving hydrogen, burning with a violet flame. At a red heat **CO** and CO_2 are decomposed, at a white heat the reverse action takes place. Liquid chlorine does not attack dry potassium (Gautier and Charpy, *C. r.*, 1891, **113**, 597). Acids attack it violently, evolving hydrogen.

2. **Occurrence.**—Very widely distributed as a portion of many silicates. In sea water in small amount as **KCl**. In numerous combinations in the large salt deposits, especially at Stassfurt: *e. g.*, carnallite, $KCl.MgCl_2 + 6H_2O$; kainite, $K_2SO_4.MgSO_4.MgCl_2 + 6H_2O$, etc. As an important constituent of many plants—grape, potato, sugar-beet, tobacco, fumaria, rumex, oxalis, etc.

3. **Preparation.** (*1*) By reduction of the carbonate with carbon. (*2*) By electrolysis of the hydroxide (Horning and Kasemeyer, *B.*, 1889, **22**, 277c; Castner, *B.*, 1892, **25**, 179c). (*3*) By reduction of K_2CO_3 or **KOH** with iron carbide: $6KOH + 2FeC_2 = 6K + 2Fe + 2CO + 2CO_2 + 3H_2$ (Castner, *C. N.*, 1886, **54**, 218). (*4*) By reduction of the carbonate or hydroxide with **Fe** or **Mg** (Winkler, *B.*, 1890, **23**, 44).

4. **Oxides** and **Hydroxide.**—*Potassium oxide*,* K_2O, is prepared by carefully

* The existence of the oxides M'_2O of **K**, **Na** and **Rb** is disputed (Erdmann and Koethner, *A.*, 1896, **294**, 55).

heating potassium with the necessary amount of oxygen (air) (Kuhnemann, *C. C.*, 1863, 491); also by heating K_2O_4 with a mixture of **K** and **Ag** (Beketoff, *C. C.*, 1881, 643). It is a hard, gray mass, melting above a red heat. Water changes it to **KOH** with generation of much heat. *Potassium hydroxide*, **KOH**, is formed by treating **K** or K_2O with water; by boiling a solution of K_2CO_3 with **Ba**, **Sr** or **Ca** oxides; by heating K_2CO_3 with Fe_2O_3 to a red heat and decomposing the potassium ferrate with water (Ellershausen, *C. C.*, 1891, (1), 1047; (2), 399). Pure water-free **KOH** is a white, hard, brittle mass, melting at a red heat. It dissolves in water with generation of much heat. *Potassium superoxide*, K_2O_4, is formed when **K** is heated in contact with abundance of air (Harcourt, *J. C.*, 1862, **14**, 267); also by bringing **K** in contact with KNO_3 heated until it begins to evolve **O** (Bolton, *C. N.*, 1886, **53**, 289). It is an amorphous powder of the color of lead chromate. Upon ignition in a silver dish oxygen is evolved and K_2O and Ag_2O formed (Harcourt, *l. c.*). Moist air or water decomposes it with evolution of oxygen. It is a powerful oxidizing agent, oxidizing **S°** to S^{VI}, **P°** to P^{V}, **K**, **As**, **Sb**, **Sn**, **Zn**, **Cu**, **Fe**, **Ag** and **Pt** to the oxides (Bolton, *l. c.*; Brodie, *Proc. Roy. Soc.*, 1863, **12**, 209).

5. **Solubilities.**—**K** and K_2O dissolve in water with violent action, forming **KOH**, which reacts with all acids forming soluble salts. Potassium dissolves in alcohol, forming potassium alcoholate and hydrogen.

Potassium platinum chloride, acid tartrate, silico-fluoride, picrate, phosphomolybdate, perchlorate, and chlorate are only sparingly soluble in cold water, and nearly insoluble in alcohol. The carbonate and sulphate are insoluble in alcohol.

6. **Reactions.** *a.*—Potassium and sodium *hydroxides* are very strong bases, fixed alkalis, and precipitate solutions of the salts of all the other metals (except **Cs**, **Rb**, and **Li**), as oxides or hydroxides. These precipitates are quite insoluble in water, except the hydroxides of **Ba**, **Sr**, and **Ca**. Excess of the reagent causes a resolution with the precipitates of **Pb**, **Sb**, **Sn**, **Al**, **Cr**, and **Zn**, forming double oxides as, K_2PbO_2, potassium plumbite, etc. Potassium *carbonate* is *deliquescent*, strongly alkaline, and precipitates solutions of the salts of the metals (except **Cs**, **Rb**, **Na**, and **Li**), forming normal carbonates with **Ag**, **Hg′**, **Cd**, **Fe″**, **Mn**, **Ba**, **Sr**, and **Ca**; oxide with **Sb**; hydroxide with **Sn**, **Fe‴**, **Al**, **Cr‴** and **Co‴**; basic salt with **Hg″**, and a basic carbonate with the other metals.

b.—The potassium salts of **HCN**, $H_4Fe(CN)_6$, $H_3Fe(CN)_6$, and **HCNS** find extended application in the detection and estimation of many of the heavy metals.

Tartaric acid, $H_2C_4H_4O_6$, or more readily sodium hydrogen tartrate, $NaHC_4H_4O_6$, precipitates, from solutions sufficiently concentrated, *potassium hydrogen tartrate*, $KHC_4H_4O_6$, granular-crystalline. If the solution be alkaline, acetic or tartaric acid should be added to strong acid reaction. The test must be made in absence of non-alkali bases. The precipitate is increased by agitation, and by addition of alcohol. It is dissolved by fifteen parts of boiling water or eighty-nine parts water at 25°, by mineral acids, by solution of borax, and by alkalis, which form the more soluble normal tartrate, $K_2C_4H_4O_6$, but not by acetic acid, or at all by alcohol of fifty per cent.

Picric acid, $C_6H_2(NO_2)_3OH$, or preferably its sodium salt, precipitates, from solutions not very dilute, the yellow, crystalline *potassium picrate*, $C_6H_2(NO_2)_3OK$, soluble in 260 parts of water at 15° C. (Reichard, Z. **40**, 25), insoluble in alcohol, by help of which it is formed in dilute solutions. The solution must be nearly neutral to avoid precipitation of the slightly soluble picric acid (soluble in 160 parts water). The dried precipitate detonates strongly when heated.

c.—If a neutral solution of a potassium salt be added to a solution of **cobaltic nitrite**,* a precipitate of the double salt *potassium cobaltic nitrite*, $K_3Co(NO_2)_6$, will be formed. In concentrated solutions the precipitate forms immediately, dilute solutions should be allowed to stand for some time; sparingly soluble in water, insoluble in alcohol and in a solution of potassium salts, hence the precipitation is more valuable as a separation of cobalt from nickel than as a test for potassium (§132, 6*c*).

Potassium nitrate is not found abundantly in nature, but is formed by the decomposition of nitrogenous organic substances in contact with potassium salts, "saltpeter plantations"; or by treating a hot solution of $NaNO_3$ with **KCl** (*D*., **2**, 2, 72). It finds extended application in the manufacture of gunpowder. *d*.—See §206, 6*d*.

e.—**Potassium sulphide** may be taken as a type of the soluble sulphides which precipitate solutions of the metals of the first four groups as sulphides except: **Hg′** becomes **HgS** and **Hg°**, **Fe‴** becomes **FeS** and **S**, and **Al** and **Cr** form hydroxides. The sulphides of arsenic, antimony and tin dissolve in an excess of the reagent, more rapidly if the alkali sulphide contain an excess of sulphur. For the general action of H_2S or soluble sulphides as a reducing agent see the respective metals. **Potassium sulphate** is used to precipitate barium, strontium, and lead. It almost always occurs in nature as double salt with magnesium, $K_2SO_4.MgSO_4.MgCl_2 + 6H_2O$, kainite, and is used in the manufacture of $KAl(SO_4)_2$, K_2CO_3 and **KOH**. As a type of a soluble sulphate it precipitates solutions of lead, mercurosum, barium, strontium, and calcium; calcium and mercurosum incompletely.

f.—**Potassium chloride** precipitates the metals of the first group, acting thus as a type of the soluble chlorides. It is much used with sodium nitrate in the preparation of potassium nitrate for the manufacture of gunpowder, in the preparation of K_2CO_3, **KOH**, and also as a fertilizer. **Potassium bromide** as a type of the soluble bromides precipitates solutions of **Pb**, **Ag**, and **Hg** (**Hg″** incompletely). **Potassium iodide** finds extended use in analytical chemistry in that it forms many soluble double iodides; it is also extensively used in medicine. As a type of a soluble iodide it precipitates solutions of the salts of **Pb**, **Ag**, **Hg**, and **Cu′**. **Cu″** salts are precipitated as **CuI** with liberation of iodine. **Fe‴** salts are merely

* One cc. of cobaltous nitrate solution and three cc. of acetic acid are added to five cc. of a ten per cent solution of sodium nitrite. This gives a yellowish solution having an odor of nitrous acid.

reduced to **Fe″** salts with liberation of iodine. Arsenic acid is merely reduced to arsenous acid with liberation of iodine.

Potassium chlorate is used as a source of oxygen and as an oxidizing agent in acid solutions. **Sodium perchlorate**, $NaClO_4$, precipitates from solutions of potassium salts *potassium perchlorate*, $KClO_4$, sparingly soluble in water and almost insoluble in strong alcohol (Kreider, *Z. anorg.*, 1895, **9**, 342). **Potassium iodate** is used as a reagent in the detection of barium as $Ba(IO_3)_2$. *g.*—The oxides of *arsenic* act as acid anhydrides toward **KOH** and form stable soluble potassium salts, arsenites and arsenates, which react with the salts of nearly all the heavy metals. *h.*—Potassium **chromate** and **dichromate** are both extensively used as reagents, especially in the analysis of **Ag**, **Pb** and **Ba** salts.

i.—**Fluosilicic** acid, H_2SiF_6, precipitates from a neutral or slightly acid solution of potassium salts, potassium fluosilicate (silico-fluoride), K_2SiF_6, soluble in 833.1 parts of water at 17.5°; in 104.8 parts at 100°; and in 327 parts of 9.6 per cent **HCl** at 14° (Stolba, *J. pr.*, 1868, **103**, 396). The precipitate is white, very nearly transparent.

j.—**Hydrochlorplatinic acid**, H_2PtCl_6, added to neutral or acid solutions not too dilute, **precipitates** *potassium chlorplatinate*, K_2PtCl_6, crystalline, *yellow*. Non-alkali bases also precipitate this reagent, and if present must be removed before this test. The precipitate is soluble in 19 parts of boiling water, or 111 parts of water at 10°. Minute proportions are detected by evaporating the solution with the reagent nearly to dryness, on the water-bath, and then dissolving in alcohol; the yellow crystalline precipitate, octahedral, remains undissolved, and may be identified under the microscope.

k.—An alcoholic solution of $BiCl_3$ in excess of $Na_2S_2O_3$ gives a yellow precipitate with solutions of potassium salts (Pauly, *C. C.*, 1887, 553). *l.*—**Gold chloride** added to sodium and potassium chloride forms chloraurates, *e.g.*, $KAuCl_4 + 2H_2O$. If these salts are dried at 100° to 110° to remove water and acids, the sodium salt is soluble in ether (separation from potassium) (Fasbender, *C. C.*, 1894, **1**, 409).

7. **Ignition.**—Ignited potassium hydroxide or potassium carbonate is a valuable desiccating agent for use in desiccators or in liquids. A mixture of molecular proportions of K_2CO_3 and Na_2CO_3 melts at a lower temperature than either of the constituents, and is frequently employed in fusion for the transposition of insoluble metallic compounds: $BaSO_4 + K_2CO_3 = BaCO_3 + K_2SO_4$.

Potassium compounds color the **flame** *violet*. A little of the solid substance, or residue by evaporation, moistened with hydrochloric acid, is brought on a platinum wire into a non-luminous flame. The wire should be previously washed with **HCl**, and held in the flame to insure the absence of potassium. The presence of very small quantities of *sodium* enables its yellow flame completely to *obscure the violet* of potassium; but owing to the greater volatility of the latter metal, flashes of violet are sometimes seen on the first introduction of the wire, or at the border of the flame, or in its base, even when enough sodium is present to conceal the violet at full heat. The interposition of a **blue glass**, or

to conceal the violet at full heat. The interposition of a **blue glass**, or prism filled with **indigo solution**, sufficiently thick, entirely cuts off the yellow light of sodium, and enables the potassium flame to be seen. The red rays of the *lithium* flame are also intercepted by the blue glass or indigo prism, a thicker stratum being required than for sodium. If organic substances are present, giving luminosity to the flame, they must be removed by ignition. Certain non-alkali bases interfere with the examination. Silicates may be fused with pure gypsum, giving vapor of potassium sulphate. Bloxam (*J. C.*, 1865, 18, 229) recommends to fuse insoluble alkali compounds with a mixture of sulphur, one part, and barium nitrate, six parts; cool, dissolve in water, remove the barium with NH_4OH and $(NH_4)_2CO_3$ and test for the alkalis as usual.

The volatile potassium compounds, when placed in the flame, give a widely-extended continuous *spectrum*, containing two characteristic lines; one line, **K** α, situated in the outermost red, and a second line, **K** β, far in the violet rays at the other end of the spectrum.

8. **Detection.**—Potassium is usually identified by the violet blue color which most of its salts impart to the Bunsen flame (7). Sodium interferes but the intervention of a cobalt glass (§**132**, 7) or a solution of indigo cuts out the yellow color of the sodium flame and allows the violet of the potassium to be seen. Some of the heavy metals interfere, hence the test should be made *after* the removal of the heavy metals (§§**211** and **212**).

Potassium may be precipitated as the platinichloride (6*j*); as the perchlorate (6*f*); as the silico-fluoride (6*i*); as the acid tartrate (6*b*); etc. Certain of these reactions are much used for the quantitative estimation (9) of potassium but are seldom used for its detection qualitatively.

9. **Estimation.**—(*1*) Potassium is converted into the sulphate or phosphate and weighed as such. (*2*) It is precipitated and weighed as the double chloride with platinum. (*3*) If present as **KOH** or K_2CO_3 it is titrated with standard acid (Kippenberger, *Z. angew.*, 1894, 495). (*4*) It is precipitated with H_2SiF_6 and strong alcohol. (*5*) Indirectly when mixed with sodium, by converting into the chlorides and weighing as such; then determining the amount of chlorine and calculating the relative amounts of the alkalis. (*6*) It is precipitated as the bitartrate in presence of alcohol and, after filtration and solution in hot water, titrated with deci-normal **KOH**. (*7*) By precipitation as the perchlorate, $KClO_4$ (Wense, *Z. angew.*, 1892, 233; Caspari, *Z. angew.*, 1893, 68).

10. **Oxidation.**—Potassium is a very powerful reducing agent, its affinity for oxygen at temperatures not too high is greater than that of any other element except **Cs** and **Rb**. For oxidizing action of K_2O_4 see 4.

§206. Sodium. Na = 23.00. Valence one.

1. **Properties.**—*Specific gravity*, 0.9735 at 13.5° (Baumhauer, *B.*, 1873, **6**, 665); 0.7414 at the boiling point (Ramsay, *B.*, 1880, **13**, 2145). *Melting point*, 97.5° (*Cir. B. of S.*, 1915). *Boiling point*, 742° (Perman, *C. N.*, 1889, **59**, 237).

A silver-white metal with a strong metallic lustre. At ordinary temperatures it is softer than **Li** or **Pb**, and can be pressed together between the fingers; at —20° it is quite hard; at 0° very ductile. It oxidizes rapidly in moist air and must be kept under benzol or kerosene. It decomposes water violently even at ordinary temperatures, evolving hydrogen, which frequently ignites from the heat of the reaction: $2Na + 2H_2O = 2NaOH + H_2$. It burns, when heated to a red heat, with a yellow flame. Pure dry **Na** is scarcely at all attacked by dry **HCl** (Cohen, *C. N.*, 1886, **54**, 17).

2. **Occurrence.**—Never occurs free in nature, but in its various combinations one of the most widely diffused metals. There is no mineral known in which its presence has not been detected. It occurs in all waters mostly as the chloride from traces in drinking waters to a nearly saturated solution in some mineral waters and in the sea water. It is found in enormous deposits as rock salt, **NaCl**; as Chili saltpeter, $NaNO_3$; in lesser quantities as carbonate, borate, sulphate, etc.

3. **Preparation.**—(*1*) By igniting the carbonate or hydroxide with carbon; (*2*) by igniting the hydroxide with metallic iron; (*3*) by electrolysis of the hydroxide; (*4*) by gently heating the carbonate with **Mg**.

4. **Oxides** and **Hydroxides.**—Sodium oxide, Na_2O, is formed by burning sodium in oxygen or in air and heating again with **Na** to decompose the Na_2O_2 (§205, 4, footnote). Sodium hydroxide, **NaOH**, is formed by dissolving the metal or the oxide in water (Rosenfeld, *J. pr.*, 1893, (2), **48**, 599); by treating a solution of sodium carbonate with lime; by fusion of $NaNO_3$ with $CaCO_3$, **CaO** and Na_2CO_3 are formed and the mass is then exhausted with water; by igniting Na_2CO_3 with Fe_2O_3, forming sodium ferrate, which is then decomposed with hot water into **NaOH** and $Fe(OH)_3$ (Solvay, *C. C.*, 1887, 829). It is a white, opaque, brittle crystalline body, melting under a red heat. The fused mass has a sp. gr. of 2.13 (Filhol, *A. Ch.*, 1847, (3), **21**, 415). It has a very powerful affinity for water, gradually absorbing water from $CaCl_2$ (Muller-Erzbach, *B.*, 1878, **11**, 409). It is soluble in about 0.47 part of water according to Bineau (*C. r.*, 1855, **41**, 509).

Sodium peroxide, Na_2O_2, is formed by heating sodium in CO_2 free air or oxygen (Prud'homme, *C. C.*, 1893, (1), 199). It reacts as H_2O_2, partly reducing and partly oxidizing. It may be fused without decomposition. Water decomposes it partially into **NaOH** and H_2O_2.

5. **Solubilities.**—Sodium and sodium oxide dissolve in water, forming the hydroxide, the former with evolution of hydrogen. In acids the corresponding sodium salts are formed, all soluble in water except sodium pyroantimonate, which is almost insoluble in water, and the fluosilicate sparingly soluble.

The nitrate and chlorate are *deliquescent*. The carbonate (10 aq), sulphate (10 aq), sulphite (8 aq), phosphate (12 aq), and the acetate (3 aq) are efflorescent.

6. **Reactions.** *a.*—As reagents sodium hydroxide and carbonates act in all respects like the corresponding potassium compounds, which see.

b.—By the greater solubility of the *picrate* and acid *tartrate* of sodium, that metal is separated from potassium (§205, 6*b*). *c.*—**Sodium nitrate** occurs in nature in large quantities as Chili saltpeter, used as a fertilizer, for the manufacture of nitric acid, with **KCl** for making KNO_3, etc.

d.—**Sodium phosphate,** Na_2HPO_4, is much used as a reagent in the precipitation and estimation of **Pb**, **Mn**, **Ba**, **Sr**, **Ca**, and **Mg**. The phosphates of all metals except the alkalis are insoluble in water (lithium phosphate is only sparingly soluble (§210, 5*c*), soluble in acids). Solu-

tions of alkali phosphates precipitate solutions of all other metallic salts as phosphates (secondary, tertiary or basic) except: $HgCl_2$ precipitates as a basic chloride (§58, 6*d*), and antimony as oxide or oxychloride (§70, 6*d*).

e, *f*, *g*, *h*.—As reagents the sodium salts react similar to the corresponding potassium salts, which see. *i*.—**Sodium fluosilicate** is soluble in 153.3 parts H_2O at 17.5° and in 40.66 parts at 100° (Stolba, *Z.*, 1872, **11**, 199); hence is not precipitated by fluosilicic acid except from very concentrated solutions (separation from **K**). *j*.—**Sodium chlorplatinate**, Na_2PtCl_6, crystallizes from its concentrated solutions in *red* prisms, or prismatic needles (distinction from potassium or ammonium). A drop of the solution to be tested is slightly acidified with hydrochloric acid from the point of a glass rod on a slip of glass, treated with two drops of solution of chlorplatinic acid, left a short time for spontaneous evaporation and crystallization, and observed under the microscope. *k*.—Sodium picrate soluble in 10 parts of water is used as a reagent for potassium salts (Richard, *Z.*, **40**, 377).

k.—Solution of **potassium pyroantimonate**, $K_2H_2Sb_2O_7$, produces in neutral or alkaline solutions of sodium salts a slow-forming, white, crystalline precipitate, $Na_2H_2Sb_2O_7$, almost insoluble in cold water. The reagent must be carefully prepared and dissolved when required, as it is not permanent in solution (§70, 4*c*).

7. **Ignition.**—Sodium bicarbonate, $NaHCO_3$, loses H_2O and CO_2 at 125° becoming Na_2CO_3, no further decomposition till 400° when a very small amount of **NaOH** is formed (Kirsling, *Z. angew.*, 1889, 332).

Sodium compounds color the flame intensely yellow, the color being scarcely affected by potassium (at full heat), but modified to orange-red by much lithium, and readily intercepted by blue glass. Infusible compounds may be ignited with calcium sulphate. The test is interfered with by some non-alkali bases, which should be removed (§§211 and 212).

The spectrum of sodium consists of a single broad band at the **D** line in the yellow of the solar spectrum separable into two bands, D_I and D_{II}, by prisms of higher refractive power.

The amount of sodium in the atmosphere, and in the larger number of substances designed to be "chemically pure" is sufficient to give a distinct but evanescent yellow color to the flame and spectrum.

8. **Detection.**—Sodium is usually detected by the color of the flame, yellow, in absence of the heavy metals. In the usual process of analysis the presence or absence of sodium is determined in the presence of magnesium (as Na_2HPO_4 is the usual reagent for the detection of magnesium, it is evident that the presence or absence of the sodium must be determined before the addition of that reagent); and as that metal gives a yellowish color to the flame it must be removed if small quantities of sodium are to be detected. For this purpose the filtrate from **Ba**, **Sr** and **Ca** is evaporated to dryness and gently ignited to expel all ammonium salts; then taken up with a small amount of water and the magnesium precipitated as the hydroxide with a solution of barium hydroxide. After

filtration the barium is removed by $(NH_4)_2CO_3$ or H_2SO_4 and the filtrate tested for sodium by the flame or by the pyroantimonate test (6*k*).

9. **Estimation.**—(*1*) If present as hydroxide or carbonate, by titration with standard acid (Lunge, *Z. angew.*, 1897, 41). (*2*) By converting into the chloride or sulphate and weighing as such. (*3*) In presence of potassium by converting into the chloride, weighing as such, then estimating the amount of chlorine with $AgNO_3$ and computing the amounts of **K** and **Na**. (*4*) It is precipitated by $K_2H_2Sb_2O_7$ and dried and weighed as $Na_2H_2Sb_2O_7$.

10. **Oxidation.**—Sodium ranks with potassium as a very powerful reducing agent. It is not quite so violent in its reaction and being much cheaper is almost universally used instead of potassium. Sodium peroxide may act both as a reducing and oxidizing agent. The action is similar to H_2O_2 in alkaline solution, which see (§**244**, 6).

§207. Ammonium. $(NH_4)'$. Valence one.

1. **Properties.**—*Specific gravity* of NH_3 gas, 0.589 (Fehling, *1*, 384); of the liquid, 0.6234 at 0° (Jolly, *A.*, 1861, **117**, 181). The liquid boils at —33.7°, at 0° the liquid has a tension of 4.8 atmospheres (Bunsen, *Pogg.*, 1839, **46**, 95). Liquid ammonia is a colorless mobile liquid, burns in air when heated or in oxygen without being previously heated. At ordinary temperature it is a gas with very penetrating odor. It burns with a greenish-yellow flame, and combines energetically with acids to form salts, the radical NH_4 being monovalent and acting in many respects similar to **K** and **Na**. At 0° one volume of water absorbs 1049.6 volumes of the gas; at 15°, 727.22 volumes (Carius, *A.*, 1856, **99**, 144). One gram of water, pressure 760 mm. and temperature 0°, absorbs 0.899 gram of NH_3; with temperature 16°, 0.578 gram (Sims, *A.*, 1861, **118**, 345).

2. **Occurrence.**—Free ammonia does not occur in nature. Various ammonium salts occur widely distributed: in rain water, in many mineral waters, in almost all plants, among the products of the decay or decomposition of nitrogenous organic bodies, etc.

3. **Preparation.**—It is obtained from the reduction of nitrates or nitrites by nascent hydrogen in alkaline solution, *e. g.*, $8Al + 5KOH + 3KNO_3 + 2H_2O = 8KAlO_2 + 3NH_3$; by the reduction with the hydrogen of the zinc-copper couple; by boiling organic compounds containing nitrogen with $KMnO_4$ in strong alkaline solution (as in water analysis); also by the oxidation of nitrogen in organic bodies with strong sulphuric (Kjeldahl method of nitrogen determination). It is prepared on a larger scale by heating an ammonium salt with lime (or some other strong base). Nearly all the ammonium hydroxide and ammonium salts of commerce are obtained as a by-product in the production of illuminating gas by the destructive distillation of coal.

4. **Hydroxide.**—Ammonium hydroxide, NH_4OH, is made by passing ammonia, NH_3, into water. The gas is absorbed by the water with great avidity, and a strongly alkaline solution is produced. A solution having a sp. gr. of 0.90 at 15° contains 28.33 per cent of NH_3 (Lunge and Wiernik, *Z. angew.*, 1889, 183).

5. **Solubilities.**—Ammonia, NH_3, and all ammonium salts are soluble in water. Ammonia dissolves less readily in a strong solution of potassium hydroxide than in water. The carbonate (acid), and phosphate are efflorescent. The nitrate and acetate are *deliquescent*, the sulphate slightly *deliquescent.*

6. **Reactions.** *a*.—The **fixed alkali hydroxides** and **carbonates** liberate ammonia, NH_3, from all ammonium salts, in the cold and more rapidly upon heating. **Ammonium hydroxide,** *volatile alkali*, colors litmus blue, neutralizes acids, forming salts, and precipitates solutions of the metals of the first four groups, manganese and magnesium salts imperfectly: due to the solubility of the hydroxide formed, in the ammonium salt produced by the reaction, and with these metals if excess of ammonium salts be present no precipitate will be formed by the NH_4OH. The precipitate is a hydroxide except: with **Ag** and **Sb** it is an oxide, with mercury a substituted ammonium salt and with lead a basic salt (see below, *k* and *l*). With salts of **Ag**, **Cu**, **Cd**, **Co**, **Ni**, and **Zn** the precipitate redissolves in excess of the reagent. **Ammonium carbonate,** $(NH_4)_2CO_3$, is unstable and used only in solution. It is formed by adding ammonium hydroxide to a solution of the acid carbonate of commerce. It precipitates solutions of all the non-alkali metals, chiefly as carbonates except magnesium salts which are not at all precipitated, as a soluble double salt is at once formed (separation of **Ba**, **Sr**, and **Ca** from **Mg**). With salts of **Ag**, **Cu**, **Cd**, **Co**, **Ni**, and **Zn**, the precipitate is redissolved by an excess of the ammonium carbonate.

b.—Dilute solutions of **picric acid** with ammonium hydroxide form intensely colored yellow solutions, a precipitate of ammonium picrate being formed if the solutions are quite concentrated. **Tartaric acid** precipitates ammonium salts very closely resembling the precipitate of potassium acid tartrate. The ammonium salt is more soluble in water than the potassium salt and does not leave K_2CO_3 upon ignition. **Sodium nitroferricyanide,** $Na_2Fe(NO)(CN)_5$, added to a mixture of NH_4OH and H_2S $[(NH_4)_2S]$ gives a very intense purple color, **characteristic** of alkali sulphides and the manipulation may be modified so as to give a very delicate test for the presence of an alkali hydroxide or of hydrosulphuric acid. In no case, however, can the H_2S be directly added to the sodium nitroferricyanide as it causes oxidation of the sulphur. To test for ammonia the gas should be liberated by **KOH** and distilled into a solution of H_2S; and this solution added to the $Na_2Fe(NO)(CN)_5$.

c.—Ammonium **nitrite,** NH_4NO_2, is used in the preparation of nitrogen (§235, 3); ammonium **nitrate** in the preparation of nitrous oxide, N_2O, "laughing gas" (§237). *d*.—Ammonium **phosphate,** as a reagent, acts similarly to sodium phosphate. When sodium phosphate, Na_2HPO_4, is used to precipitate metals in the presence of ammonium hydroxide, a double phosphate of the metal and ammonium is frequently formed as $MnNH_4PO_4$, $MgNH_4PO_4$, etc. By some chemists microcosmic salt, $NaNH_4HPO_4$, is preferred to sodium phosphate, Na_2HPO_4, as a reagent.

e.—When ammonium hydroxide is saturated with H_2S, *ammonium sulphide,* $(NH_4)_2S$, is formed. Complete saturation is indicated by the failure

to precipitate magnesium salts, that is, NH_4OH precipitates magnesium salts while $(NH_4)_2S$ does not. Freshly prepared ammonium sulphide is colorless, but upon standing becomes yellow with loss of ammonia and formation of the poly-sulphides, $(NH_4)_2S_x$. The yellow poly-sulphide may also be formed by dissolving sulphur in the normal ammonium sulphide. As a precipitant *ammonium sulphide* acts similarly to the fixed alkali sulphides. The sulphides of Sb‴ and Sn″ are with great difficulty soluble in the normal ammonium sulphide, but readily soluble in the poly-sulphide. Nickel sulphide, NiS, is insoluble in normal ammonium sulphide but is sparingly soluble in the yellow poly-sulphide (distinction from cobalt). $(NH_4)_2S$ gives a rich purple color with sodium nitroferricyanide (*b*). **Ammonium sulphate** as a precipitating reagent acts similar to all soluble sulphates (§205, 6*e*). A 25 per cent solution of $(NH_4)_2SO_4$ is used to dissolve $CaSO_4$ (§188, 5*c*) (distinction from Ba and Sr).

f.—**Ammonium chloride** is much used as a reagent. It prevents precipitation of the salts of Mn by the NH_4OH, and is of special value in the precipitation of the third group as hydroxides and the fourth group as sulphides by preventing the formation of soluble colloidal compounds. The solubility of the precipitates of the carbonates of the fifth group is slightly increased by the presence of ammonium chloride; *i. e.*, very dilute solutions of barium chloride are not precipitated by ammonium carbonate in presence of a large excess of ammonium chloride. The salts of magnesium are not precipitated by the alkalis or by the alkali carbonates in presence of ammonium chloride. The solubility of $Al(OH)_3$ is diminished by the presence of NH_4Cl (§124, 6*a*, and §117).

g, *h*.—Similar as reagents to the corresponding potassium salts. *i*.—**Fluosilicic acid**, H_2SiF_6, does not precipitate ammonium salts, the ammonium fluosilicate being very soluble in water (distinction from potassium). *j*.—Chlorplatinic acid, H_2PtCl_6, forms with ammonium salts the yellow ammonium chlorplatinate, $(NH_4)_2PtCl_6$, very closely resembling the potassium salt with the same reagent, but upon ignition only the spongy metallic platinum is left, *i. e.*, no chloride of the alkali metal, as KCl.

k.—A solution of **potassium mercuric iodide**, K_2HgI_4, containing also potassium hydroxide—**Nessler's test** *—produces a brown precipitate of nitrogen dimercuric iodide, NHg_2I, dimercur-ammonium iodide (§58, 6*a*), soluble by excess of KI and by HCl; not soluble by KBr (distinction from HgO):

$$NH_3 + 2HgI_2 = NHg_2I + 3HI$$
$$NH_4OH + 2K_2HgI_4 + 3KOH = NHg_2I + 7KI + 4H_2O$$

* This reagent may be prepared as follows: To a solution of mercuric chloride add solution of potassium iodide till the precipitate is nearly all redissolved; then add solution of potassium hydroxide sufficient to liberate ammonia from ammonium salts; leave until the liquid becomes clear, and decant from any remaining sediment.

This very delicate test is applicable to ammonium hydroxide or salts; traces forming only a yellow to brown coloration. The potassium mercuric iodide, "Meyers Reagent," alone, precipitates the *alkaloids* from *neutral or acid* solutions, but does not precipitate ammonium salts from neutral or acid solutions. Ammonium hydroxide in alcoholic solution does not give a precipitate with Nessler's reagent, but from this solution a precipitate is formed with $HgCl_2$ (De Koninck, *Z.*, 1893, **32**, 188).

l.—**Mercuric chloride, $HgCl_2$,** forms, in solutions of ammonium hydroxide or ammonium carbonate, the "white precipitate" of nitrogen dihydrogen mercuric chloride, NH_2HgCl, or mercur-ammonium chloride. If the ammonium is in a salt, not carbonate, it is changed to the carbonate and precipitated, by addition of mercuric chloride and potassium carbonate previously mixed in solutions (with pure water), so dilute as not to precipitate each other (yellow). This test is intensely delicate, revealing the presence of ammonia derived from the air by water and many substances (Wittstein, *Arch. Pharm.*, 1873, **203**, 327).

m.—Add a small quantity of recently precipitated and well-washed **silver chloride**, and, if it does not *dissolve* after agitation, then add a little potassium hydroxide solution. The solution of the **AgCl**, *before* the addition of the fixed alkali, indicates free ammonia; *after* the addition of the fixed alkali, ammonium salt. (Applicable in absence of thiosulphates, iodides, bromides and sulphocyanates.)

n.—**Sodium phosphomolybdate** (§75, 6*d*) precipitates ammonium from neutral or acid solutions; also precipitates the alkaloids, even from very dilute solutions, and, from concentrated solutions, likewise precipitates **K**, **Rb** and **Cs** (all the fixed alkalis except **Na** and **Li**).

7. **Ignition.**—Heat vaporizes the carbonate, and the haloid salts of ammonium, undecomposed (dissociated but reuniting upon cooling); decomposes the nitrate with formation of nitrous oxide and water, and the phosphate and borate with evolution of ammonia. NH_3 heated to 780° or higher is dissociated into **N** and **H** (Ramsay and Young, *J. C.*, 1884, **45**, 88).

8. **Detection.**—As ammonium hydroxide and chloride are used in the regular process of analysis, the original solution must be tested for the presence or absence of ammonium compounds. The hydroxide or the carbonate may be detected by the odor (1); the action on red litmus paper suspended in the test-tube above the heated solution; the blue color imparted to paper wet with copper sulphate; the blackening of mercurous nitrate paper; and if in considerable quantity, the white vapors when brought into contact with the vapors of volatile acids. In combination as salts the gas is liberated by the fixed alkali hydroxides or carbonates (oxides or hydroxides of **Ba**, **Sr**, or **Ca** may be used) and distilled into Nessler's reagent, or collected in water and the test with $HgCl_2$ (6*l*) applied or any of the tests for ammonium hydroxide.

9. **Estimation.**—**Ammonium** salts are usually estimated by distillation into a standard acid, from a solution made alkaline with **KOH**, and titration of the excess of the acid with a standard NH_4OH solution, using tincture of cochineal

as an indicator. It may be converted into the chloride and precipitated by $PtCl_4$ and weighed as the double platinum salt.

10. **Oxidation.**—Ammonium salts in solution, treated with *chlorine* gas, generate the unstable and violently explosive "nitrogen chloride" (NCl_3?) (*a*). The same product is liable to arise from solid ammonium salts treated with chlorine. Gaseous ammonia, and ammonium hydroxide, with chlorine gas, generate free nitrogen (*b*), a little ammonium chlorate being formed if the ammonia is in excess. *Hypochlorites* or *hypobromites* (or chlorine or bromine dissolved in aqueous alkali, so as to leave an alkaline reaction) liberate, from dissolved ammonium salts, all of their nitrogen (as shown in the second equation of *b*); the measure of the nitrogen gas being a means of quantitative estimation of ammonium. With iodine, ammonium iodide and the explosive iodamides (*c*) are produced; or under certain conditions an iodate (*d*). Ammonium hydroxide is liable to atmospheric oxidation to ammonium nitrite and nitrate. Permanganates oxidize to nitrate (*e*) (Wanklyn and Gamgee, *J. C.*, 1868, **21**, 29). In presence of **Cu** the **O** of the air oxidizes the nitrogen of ammonia to a nitrite (*f*) (Berthelot and Saint-Gilles, *A. Ch.*, 1864, (4), **1**, 381). Ammonia is somewhat readily produced from nitric acid by strong reducing agents (*g*). It is formed with carbonic anhydride, in a water solution of cyanic acid, and, more slowly, in a water solution of hydrocyanic acid. It is generated, by fixed alkalis, in boiling solution of cyanides (*h*); also in boiling solutions of albuminoids and other nitrogenous organic compounds, this formation being hastened and increased by addition of permanganate (Wanklyn's process). Fusion with fixed alkalis transforms all the nitrogen of organic bodies into ammonia.

(*a*) $NH_4Cl + 3Cl_2 = NCl_3 + 4HCl$

(*b*) $8NH_3 + 3Cl_2 = 6NH_4Cl + N_2$

$2NH_4Cl + 3Cl_2 = 8HCl + N_2$

(*c*) $2NH_3 + I_2 = NH_4I + NH_2I$

(*d*) $6NH_4OH + 3I_2 = 5NH_4I + NH_4IO_3 + 3H_2O$

(*e*) $6NH_4OH + 8HMnO_4 = 3NH_4NO_3 + 8MnO(OH)_2 + 5H_2O$

(*f*) $12Cu + 2NH_3 + 9O_2 = 12CuO + 2HNO_2 + 2H_2O$

(*g*) $3HNO_3 + 8Al + 8KOH = 8KAlO_2 + 3NH_3 + H_2O$

(*h*) $HCN + KOH + H_2O = NH_3 + KCHO_2$ (formate).

§208. Caesium. Cs = 132.81. Valence one.

1. **Properties.**—*Specific gravity*, 1.88 at 15° (Setterberg, *A.*, 1882, **211**, 100). *Melting point*, between 26° and 27°. It is quite similar to the other alkali metals; silver-white, ductile, very soft at ordinary temperature. It burns rapidly when heated in the air, and takes fire when thrown on water. It may be kept under petroleum. It is the most strongly electro-positive of all metals.

2. **Occurrence.**—Widely distributed but in small quantities; as caesium aluminum silicate (mineral castor and pollux) (Pisani, *C. r.*, 1864, **58**, 715); in many mineral springs (Miller, *C. N.*, 1864, 10, 181); in the ash of certain plants, tobacco, tea, etc.

3. **Preparation.**—By electrolysis of a mixture of **CsCN** with $Ba(CN)_2$; by ignition of **CsOH** with **Al** in a nickel retort (Beketoff, *C. C.*, 1891, (2), 450).

4. **Oxide** and **Hydroxide.**—An oxide has not yet been prepared. The hydroxide, **CsOH**, is a grayish-white solid, very *deliquescent*, absorbs CO_2 from the air; dissolves in water with generation of much heat, forming a strongly caustic solution.

5. **Solubilities.**—Caesium dissolves with great energy in water, acids or alcohol, liberating hydrogen and forming the hydroxide, salts or alcoholate respectively. The hydroxide is soluble in water and alcohol. The salts are all quite readily soluble; the double platinum chloride, Cs_2PtCl_4, and the acid tartrate, $CsHC_4H_4O_6$, being least soluble and used in preparation of the salts free from the other alkali metals.

6. **Reactions.**—In all its reactions similar to the other fixed alkalis.

7. **Ignition.**—Caesium salts color the non-luminous flame violet. The spectrum gives two sharply defined lines, **Cs** α and **Cs** β, in the blue and a third faint line in the orange-red **Cs** γ, also several faint lines in the yellow and green. With the spectroscope three parts of **CsCl** may be detected in presence of 300,000 to 400,000 parts **KCl** or **NaCl**; and one part in presence of 1,500,000 parts **LiCl** (Bunsen, *Pogg.*, 1875, **155**, 633).

8. **Detection.**—By the spectroscope (7 and §210, 7).

9. **Estimation.**—(*1*) As the double platinum chloride; (*2*) as the chloride with **RbCl**, estimation of the amount of **Cl** and calculation of the relative amounts of the metals; (*3*) as the sulphate obtained from ignition of the acid tartrate and treatment with H_2SO_4 (Bunsen, *Pogg.*, 1863, **119**, 1).

§209. Rubidium. Rb = 85.45. Valence one.

1. **Properties.**—*Specific gravity*, 1.52 (Bunsen, *A.*, 1863, **125**, 367). *Melting point*, 38° (*Cir. B. of S.*, 1915); at −10° soft as wax. A lustrous silver-white metal with a tinge of yellow, oxidizes rapidly in the air, developing much heat and soon igniting. Volatile as a blue vapor below a red heat. The metal does not keep well under petroleum, but is best preserved in an atmosphere of hydrogen. Next to caesium it is the most electro-positive of all metals.

2. **Occurrence.**—Widely distributed in small quantities, usually with caesium, and frequently with the other alkali metals, always in combination. None of the alkali metals can occur free in nature.

3. **Preparation.**—From the mother liquor obtained in the preparation of **Li** salts (Heintz, *J. pr.*, 1862, **87**, 310): (*1*) By ignition of the acid tartrate with charcoal; (*2*) electrolysis of the chloride; (*3*) by ignition with **Mg** or **Al** (Winkler, *B.*, 1890, **23**, 51; Beketoff, *B.*, 1888, **21**, c, 424).

4. **Oxide** and **Hydroxide.**—The oxide Rb_2O has not been with certainty prepared. The hydroxide, **RbOH**, is formed when the metal is decomposed by water; also through the action of $Ba(OH)_2$ upon Rb_2SO_4. It is a gray-white, brittle mass, melting under a red heat.

5. **Solubilities.**—The metal dissolves in cold water, in acids and in alcohol with great energy, evolving hydrogen. The hydroxide is readily soluble in water with generation of heat. The salts are all quite readily soluble. The acid tartrate is about eight times less soluble than the corresponding **Cs** salt. Among the less soluble salts are to be mentioned the perchlorate, the fluosilicate, the double platinum chloride, the silicotungstate, the pierate, and the phosphomolybdate. The alum is less soluble than the corresponding potassium alum.

6. **Reactions.**—Similar to the other fixed alkalis.

7. **Ignition.**—The salts give a violet color to the flame. The spectrum gives two characteristic lines in the violet, **Rb** α and **Rb** β; two less intensive in the outer red, **Rb** γ and **Rb** δ; a fifth **Rb** ε in the orange; and many faint lines in the orange, yellow and green. As small a quantity as 0.0000002 gram of **RbCl** can be detected (Bunsen, *l. c.*).

8. **Detection.**—By the spectroscope (7 and §210, 7).

9. **Estimation.**—(*1*) By weighing with **CsCl** as the chlorides, determining the amount of **Cl** and calculating the proportion of the metals; (*2*) as the double platinum chloride.

§210. Lithium. Li = 6.94. Valence one.

1. **Properties.**—*Specific gravity*, 0.5936, the lightest of all known solid bodies (Bunsen and Matthiessen, *A.*, 1855, **94**, 107). *Melting point*, 186° (*Cir. B. of S.*, 1915); does not vaporize at a red heat. It is a silver-white metal with a grayish tinge; harder than **K** or **Na**, but softer than **Pb**, **Ca** or **Sr**; it is tough and may be drawn into wire and rolled into sheets. It is more electro-positive than the alkaline earth metals, but less electro-positive than **K** or **Na**. The pure metal is quite similar in appearance and in its chemical properties to **K**

and **Na**, but does not react so violently as those metals. It does not ignite in the air until heated to 200°, and then burns quietly with a very intense white light. It also burns with vivid incandescence in **Cl**, **Br**, **I**, **O**, **S** and dry CO_2. It decomposes water readily, forming **LiOH** and **H**, but not with combustion of the hydrogen or ignition of the metal.

2. **Occurrence.**—It is a sparingly but widely distributed metal, usually prepared from lepidolite, triphylite, or petalite. Traces are found in a great many minerals, in mineral springs, and in the leaves and ashes of many plants; *e. g.*, coffee, tobacco and sugar-cane.

3. **Preparation.**—It is prepared pure only by electrolysis, usually of the chloride. A larger yield is obtained by mixing the **LiCl** with NH_4Cl or **KCl** (Güntz, *C. r.*, 1893, **117**, 732). The metal is also obtained by ignition of the carbonate with **Mg**, but the metal is at once vaporized and oxidized.

4. **Oxide** and **Hydroxide.**—It forms one oxide, Li_2O, by heating the metal in oxygen or dry air; cheaper by the action of heat upon the nitrate. The corresponding hydroxide, **LiOH**, is made by the action of water upon the metal or its oxide; cheaper by heating the carbonate with calcium hydroxide.

5. **Solubilities.**—The metal is readily soluble in water with evolution of hydrogen, forming the hydroxide; soluble in acids with formation of salts. The oxide, Li_2O, dissolves in water, forming the hydroxide. The most of the lithium salts are soluble in water. A number of the salts, including the chloride and chlorate, are very *deliquescent*. The hydroxide, carbonate and phosphate are less soluble in water than the corresponding compounds of the other alkali metals. In this respect lithium shows an approach to the alkaline earth metals. **LiOH** is soluble in 14.5 parts water at 20° (Dittmar, *J. Soc. Ind.*, 1888, **7**, 730); Li_2CO_3 in 75 parts at 20°; Li_3PO_4 in 2539 parts pure water and 3920 parts ammoniacal water, more soluble in a solution of NH_4Cl than in pure water (Mayer, *A.*, 1856, **98**, 193). Lithium chloroplatinate and lithium picrate are very soluble in water (Richard *Z.*, **40**, 383).

6. **Reactions.**—Lithium salts in general react similar to the corresponding potassium and sodium salts. They are as a rule more fusible and more easily decomposed upon fusion. Soluble **phosphates** precipitate *lithium phosphate*, more soluble in NH_4Cl solution than in pure water (distinction from magnesium). In dilute solutions the phosphate is not precipitated until the solution is boiled. The delicacy of the test is increased by the addition of **NaOH**, forming a double phosphate of **Na** and **Li** (Rammelsberg, *A. Ch.*, 1818, (2), **7**, 157). The phosphate dissolved in **HCl** is not at once precipitated by neutralizing with NH_4OH (distinction from the alkaline earth metals). Nitrophenic acid forms a yellow precipitate, not easily soluble in water.

7. **Ignition.**—Compounds of lithium impart to the **flame** a carmine-*red* color, obscured by sodium, but not by small quantities of potassium compounds. Blue glass, just thick enough to cut off the yellow light of sodium, transmits the red light of lithium; but the latter is intercepted by a thicker part of the blue prism, or by several plates of blue glass. The **spectrum** of lithium consists of a bright red band, **Li** α, and a faint orange line, **Li** β. The color tests have an intensity intermediate between those of sodium and potassium.

8. **Detection.**—*By the spectroscope.*—To the dry chlorides of the alkali metals a few drops of **HCl** are added and the mass extracted with 90 per cent alcohol. The solution contains all the rare alkalis and some **Na** and **K**. Evaporate to dryness, dissolve in a small amount of water and precipitate with platinum chloride. The double platinum and potassium chloride is more soluble than the corresponding salt of **Rb** and **Cs**. Boil repeatedly with small portions of water to remove the potassium, and frequently examine the residue by the spectroscope as follows: Wrap a small amount of the precipitate in a moistened filter paper, then in a platinum wire and carefully char. After charring is complete, ignite before the spectroscope. The **K** spectrum grows fainter, that of **Rb** and **Cs** appear.

Evaporate to dryness the filtrate from the precipitate of the platinum double salts, add oxalic acid and ignite, moisten with **HCl**, evaporate and extract with absolute alcohol and ether. Upon evaporation of the extract **LiCl** is obtained, almost pure. Test with the spectroscope and by forming the insoluble phosphate.

9. **Estimation.**—After separation from other elements it may be weighed as a sulphate, carbonate or phosphate, Li_3PO_4. It may also be estimated by the comparative intensity of the lines in the spectroscope (Bell, *Am.*, 1886, **7**, 35).

Directions for the Analysis of the Metals of the Alkali Group (Sixth Group).

§**211.** If the material is found not to contain magnesium, the clear filtrate from the carbonates of **Ba**, **Sr**, and **Ca**, after testing for traces with $(NH_4)_2SO_4$ and $(NH_4)_2C_2O_4$ (§**193**), may at once be tested for the **presence of potassium and sodium.** If magnesium be present it should be removed in order to test for small amounts of sodium. Potassium and large amounts of sodium may be readily detected in the presence of magnesium. It is evident that the magnesium must not be removed by the usual reagent used to detect the presence of that element, *i. e.* Na_2HPO_4. It is recommended by many to use ammonium phosphate, $(NH_4)_2HPO_4$. This reagent removes the magnesium, and permits the application of the flame test for the fixed alkalis; but the presence of the phosphate obstructs the gravimetric determination of the alkalis. The phosphate may be removed by lead acetate and the excess of the lead by hydrogen sulphide.

§**212.** As a better method it is directed to evaporate the filtrate containing the magnesium and the alkalis to dryness, ignite gently to remove the ammonium salts. Dissolve the residue in water and add $Ba(OH)_2$ to precipitate the magnesium as $Mg(OH)_2$ (§§**177** and **182**). After filtration, the excess of barium in the filtrate is removed by H_2SO_4, and the filtrate from the barium sulphate is ready to be tested for the fixed alkalis by the flame test or by gravimetric methods as may be desired. The presence of sodium obscures the flame reaction for potassium, but the introduction of a cobalt glass (§**132**, 7) or an indigo prism cuts out the sodium flame and allows the violet potassium flame to be seen. Study 6, 7, 8, and 9 of §§**205** and **206**.

§**213.** The free use of ammonium salts during the process of analysis makes it necessary that the testing for **ammonium** be done in the **original solution** or in the filtrate from the Tin and Copper Group.

Add an excess of **KOH** or **NaOH** to the solution and warm gently. Notice the odor (§**207**, 1). Suspend a piece of moistened red litmus paper in the test-tube; in the presence of ammonia it will be changed from red to blue color. To detect the presence of small amounts of ammonium salts, heat the strongly alkaline mixture nearly to boiling and pass the evolved gas into water. Test this solution (ammonium hydroxide) with Nessler's Reagent (§**207**, 6*k*) or by the precipitation with $HgCl_2$ (§**207**, 6*l*). Study §**207**, 6, 7, 8, and 9.

§**214.** The rare metals of the Alkali Group: lithium, rubidium, and

caesium, are rarely met with in the ordinary analyses. If their presence is suspected they are tested for and detected by the spectroscope (7, §§**208, 209** and **210**).

§**215.** Lithium, because of the insolubility of its phosphate (§**210,** 5*c*), interferes with the detection of magnesium. If the filtrate after the removal of barium, strontium, and calcium be evaporated to dryness and gently ignited to remove all ammonium salts, the residue, dissolved in water and treated with an excess of barium hydroxide, will give a precipitate of the magnesium as the hydroxide, leaving the lithium in solution. The barium hydroxide precipitate may be tested for magnesium and from the filtrate the excess of barium hydroxide may be removed by sulphuric acid before testing for the alkali metals.

PART III.–THE NON-METALS.

§216. Balancing Equations in Oxidation and Reduction.

Oxidation and reduction always involves a change in valence. When the valence of an electropositive element is increased it is said to be oxidized, and conversely, when its valence is reduced, reduction has taken place. It is believed that each bond or valence is produced by the presence of a unit charge of electricity on the atom or ion. A ferrous ion may be represented as Fe^{++} while a ferric ion would be Fe^{+++} and the oxidation or reduction of iron would therefore consist in adding to or subtracting a unit charge of electricity from the atom. Similarly the valence of negative elements is proportional to the number of negative charges of electricity on their atoms. It is assumed that during oxidation and reduction unit charges of negative electricity carried by small corpuscles or electrons pass from one atom to the other. The positively charged masses of atoms are very much larger than the negative electrons. When an atom loses a negative electron, its positive charge is relatively increased and it is oxidized; when it gains a negative electron it is reduced.

The valence of an electro-negative element would therefore be increased when it is reduced and reduced when it is oxidized. When an element can pass from the positive to the negative condition there may be no change in valence during reduction or oxidation. $2N_2^{-}H_3^{+} + 3O^{=} = N_2^{+++}O_3^{=} + 3H_2O$.

The metals in salts generally act as electro-positive elements while the acid elements or radicles are electro-negative. The latter therefore may act as oxidizing agents towards the former. In general in a reaction involving oxidation and reduction one element is oxidized and another is reduced and the gain in valence of one element is exactly equal to the loss in valence of the other element. This is a necessary consequence of the transfer of negative electrons from one element to the other.

Statement of Bonds in Plus and Minus Numbers,* according to chemical polarity, positive and negative (see §3 footnote).

A bond, that is a unite of *active* valence, is either a plus one or a minus one. The formula of a molecule of hydrochloric acid is stated, $H^{+1}Cl^{-1}$,

* O. C. Johnson, *C. N.*, 1880, 42, 51. See also Ostwald, *Grundr. allg.Chem.*, 3te Aufl., 1899, S. 439.

that of water, $(H^{+I})_2O^{-II}$. (The plus sign is understood when no sign is written before the valence number.)

Plus and minus bonds are represented as positive and negative quantities. In the formula of hydrochloric acid, as above, the difference between the polarity of the hydrogen atom and that of the chlorine atom is stated as a difference of two.

In any compound *the sum* of the plus bonds and the minus bonds of the atoms forming a molecule is zero.

Free elements, not having *active* valence, have zero bonds in this notation.*

The Oxidation of any element is shown by an increase, and its Reduction by a decrease, in the sum of its bonds.

When one substance reduces another the element which is reduced loses as many bonds as are gained by the element which is oxidized.

It is evident that, changes in valence being reciprocal in oxidation and reduction, there is no gain or loss in *the sum* of the bonds of two elements which act upon each other.

The use of this notation is illustrated in the following equations:

$$3SnCl_2 + H_2SO_3 + 6HCl = 3SnCl_4 + H_2S + 3H_2O$$

In this equation the three atoms of tin gain six bonds; the bonds of the sulphur in the H_2SO_3 have then been diminished by six; that is, it has given up six bonds to the tin, and having only four in the first place must now have minus two $(4 - 6 = -2)$.

The valence of the acid element in an acid may always be found from the anhydride. In this case we have: $H_2SO_3 = SO_2 + H_2O$, the valence of the sulphur in SO_2 being 4.

$$3\overset{++}{Sn}Cl_2 + HIO_3 + 6HCl = 3\overset{++++}{Sn}Cl_4 + HI + 3H_2O$$

Here also the three atoms of tin gain six bonds, and these are furnished by the iodine of the HIO_3. It has five in the first place, and being diminished by six, has one negative bond remaining $(5 - 6 = -1)$. [In other words, unless we deny that iodine has five bonds in HIO_3, we must admit that it has one negative bond in HI (written $H'I^{-'}$).]

$$8HMnO_4 + 5AsH_3 + 8H_2SO_4 = 5H_3AsO_4 + 8MnSO_4 + 12H_2O$$

In this equation eight atoms of manganese in the first member have 56 bonds, and a like amount in the second member has only 16, losing 40, and this 40 has been gained by the five atoms of arsenic. They now have

* If there is polarity in the union of like atoms with each other in forming an elemental molecule, the sum must be zero, as in the formation of the molecules of compounds.

25, after gaining 40. They must then have had — 15 in the first place (25 — 40 = −15). That is, the atom of arsenic in arsenous hydride has −3 bonds ($As^{-'''}H_3$).

$$SnCl_2 + HgCl_2 = Hg + SnCl_4$$

This equation illustrates the statement that free elements have no bonds. The tin gains two bonds, and these two bonds are taken from the mercury in the $HgCl_2$.

§217. Rule for Balancing Equations.

The number of oxidation bonds which any element has is determined by the following rules:

a. Hydrogen has always one positive bond.

b. Oxygen has always two negative bonds.

c. Free elements have no bonds.

d. The sum of the bonds of any compound is zero.

e. In salts the bond of the metal is always positive.

f. In acids and in salts the acid radical has always negative bonds.

Thus, the bond of free **Pb** is zero, but in $PbCl_2$ the lead has two positive bonds, and each atom of chlorine has one negative bond.

In Bi_2S_3, each atom of **Bi** has three positive bonds (*e*), and each atom of **S** has two negative bonds (*f*).

In the following salts, etc., the bond of each element is marked above, with its proper sign, plus being understood if no sign is given. Then follows the equation in full, the bonds of each atom being multiplied by the number of atoms, and all being added, the sum is seen to be zero.

$$Hg''(N^{V}O^{-''}_3)_2.2 + 10 - 12 = 0$$
$$Bi'''_3(S^{VI}O^{-''}_4)_3.6 + 18 - 24 = 0$$
$$Ba''(Mn^{VII}O^{-''}_4)_2.2 + 14 - 16 = 0$$
$$Fe'''(N^{V}O^{-''}_3)_3.3 + 15 - 18 = 0$$
$$As'''_2S^{-''}_3.6 - 6 = 0$$

If the above is understood, the rule for balancing equations is easily explained.

The number of bonds changed in one molecule of each shows the number

of the molecules of the other which must be taken, the words *each* and *other* referring to the oxidizing and reducing agents.

§218. A few equations will illustrate the application of the rule.

(*1*) $3As_4 + 20HNO_3 + 8H_2O = 12H_3AsO_4 + 20NO$

The arsenic in one molecule gains 20 bonds, therefore 20 molecules of HNO_3 are taken. The nitrogen loses three bonds, therefore three molecules of As_4 are taken. The valence of the nitrogen and arsenic may be found from their anhydrides:

$$2HNO_3 = H_2O + N_2O_5 \quad \text{and} \quad 2H_3AsO_4 = 3H_2O + As_2O_5$$

Equations of this kind may also be balanced by considering that the arsenic must be oxidized to the pentoxide, one molecule of arsenic requiring ten atoms of oxygen. Two molecules of nitric acid furnish three atoms of oxygen, as follows:

$$2HNO_3 = H_2O + 2NO + 3O$$

Three molecules of arsenic must, therefore, be taken, requiring thirty atoms of oxygen, which will be furnished by 20 molecules of nitric acid. To convert a molecule of arsenic pentoxide into arsenic acid requires 3 molecules of water. The 3 molecules of arsenic will therefore require 18 molecules of water. As the 20 molecules of nitric acid furnish 10 molecules of water, 8 more must be added.

(*2*) $6Sb + 10HNO_3 = 3Sb_2O_5 + 10NO + 5H_2O$

The antimony gains five bonds, therefore five molecules of HNO_3 would be taken, and since the nitrogen loses three bonds, three of antimony would be taken, but since we cannot write Sb_2O_5 with an odd number of atoms of antimony, we double the ratio and take six and ten.

(*3*) $3H_2S + 8HNO_3 = 3H_2SO_4 + 8NO + 4H_2O$

The **S** in the first member has 2 negative bonds (*a* and *d*); in the second member it has 6 positive, gaining 8 bonds; hence 8 molecules of HNO_3 must be taken. The nitrogen in the first member has five bonds, and in the second it has two. The difference is three, therefore just three molecules of H_2S must be taken.

Further, the reaction may be explained as follows:

The sulphur in the first member has two bonds (valence of two), but negative because combined with hydrogen (two atoms) to form a definite compound; in the second member it has six bonds (valence of six), but positive because combined with oxygen (SO_3 or $\begin{matrix} HO- \\ HO- \end{matrix}\!\!S\begin{matrix} =O \\ =O \end{matrix}$). The valence of the hydrogen does not change and hence in the reaction one molecule of H_2S gains eight bonds. The nitrogen in the first member has five bonds (valence of five), but positive because combined with oxygen (N_2O_5 or $H-O-N\begin{matrix} =O \\ =O \end{matrix}$); in the second member it has two bonds, still positive because combined with oxygen. The valence of the hydrogen and oxygen does not change, hence in the reaction one molecule of HNO_3 loses three bonds. Now the number of bonds gained by the H_2S (*8*) must equal the bonds lost by the HNO_3 (*3*). The least common multiple, twenty-four, indicates the least possible total change of valence for each compound; this requires that three molecules of H_2S and eight of HNO_3 be taken, giving for the products three molecules of H_2SO_4 and eight of **NO** with four of water to complete the equation.

(*4*) $3Sb_2S_3 + 28HNO_3 = 3Sb_2O_5 + 9H_2SO_4 + 28NO + 5H_2O$

In this case, both the **Sb** and the **S** in the molecule gain bonds, and must be

considered. It is plain (from *d* and *e*) that each atom of **Sb** gains 2 bonds, and the two in the molecule will gain 4.

The **S** in Sb_2S_3 has 2 negative bonds, and in the second member (in H_2SO_4) it has 6 positive bonds, a gain of 8. The three atoms in the molecule will gain three times eight, or 24 bonds; to this add the 4 which the **Sb** has gained, and we have 28 bonds gained by one molecule of Sb_2S_3; hence 28 molecules of HNO_3 must be taken. We take 3 of Sb_2S_3 for reasons explained in the first equation.

Further explain as follows: In this case both the **Sb** and the **S** gain in valence (oxidized). Each atom of antimony gains two bonds, a total gain of four. Each atom of sulphur gains eight, a total gain of twenty-four; or a gain for one molecule of Sb_2S_3 of twenty-eight bonds. As in the previous illustration, the nitrogen loses three bonds. The least common multiple, eighty-four, indicates that for the reaction each compound must undergo a change of at least eighty-four bonds. This requires for the Sb_2S_3 three molecules, and for the HNO_3 twenty-eight molecules. The products are as indicated in the equation.

(*5*) $2Ag_3AsO_4 + 11Zn + 11H_2SO_4 = 2AsH_3 + 6Ag + 11ZnSO_4 + 8H_2O$

The silver loses three bonds, and the arsenic in changing from plus five to minus three loses eight bonds; this added to the three that the silver loses makes eleven, therefore eleven atoms of zinc are taken, and since the zinc gains two, two molecules of silver arsenate are taken.

(*6*) $2MnO + 5Pb_3O_4 + 30HNO_3 = 2HMnO_4 + 15Pb(NO_3)_2 + 14H_2O$

The manganese gains five bonds, therefore five molecules of Pb_3O_4 are taken. The three atoms of lead in one molecule of Pb_3O_4 have in all eight bonds, but a like amount has only six in the second member, being a loss of two, therefore two molecules of **MnO** are taken.

(*7*) $2MnBr_2 + 7PbO_2 + 14HNO_3 = 2HMnO_4 + 2Br_2 + 7Pb(NO_3)_2 + 6H_2O$

The manganese gains five bonds and the bromine gains one, the two atoms gaining two, adding this to the five that the manganese gains makes a total gain of seven bonds, therefore seven of PbO_2 are taken. The lead loses two, therefore two of $MnBr_2$ are taken.

(*8*) $MnS + 4KNO_3 + K_2CO_3$, fusion $= K_2MnO_4 + K_2SO_4 + 4NO + K_2CO_3$

The manganese gains four bonds and the sulphur eight, making twelve; therefore twelve of KNO_3 would be taken, and since the nitrogen loses three bonds, three of **MnS** would be taken, but since three is to twelve as one is to four, the latter amounts are taken.

(*9*) $2Cr(OH)_3 + 3Mn(NO_3)_2 + 5K_2CO_3$, fusion $= 2K_2CrO_4 + 3K_2MnO_4 + 6NO + 5CO_2 + 3H_2O$

This is a peculiar and instructive equation. The nitrogen loses six bonds, but since the manganese in the same molecule gains four, the total loss is only two, therefore two of $Cr(OH)_3$ are taken. The chromium gains three, therefore three of $Mn(NO_3)_2$ are taken.

(*10*) $3Ag + 4HNO_3 = 3AgNO_3 + NO + 2H_2O$

The rule here calls for three of silver and one of nitric acid, but three more of unreduced nitric acid are needed to combine with the silver, making four in all.

(*11*) $2FeI_2 + 6H_2SO_4$, conc., hot $= Fe_2(SO_4)_3 + 3SO_2 + 2I_2 + 6H_2O$

The rule here calls for two of FeI_2 and three of H_2SO_4, but three more of H_2SO_4 that are not reduced are needed to combine with the iron, making six in all.

(*12*) $3HNO_3 + 8Al + 8KOH = 3NH_3 + 8KAlO_2 + H_2O$

The nitrogen has five bonds in HNO_3, and in NH_3 it has minus three, losing eight, therefore eight of aluminum are taken. The aluminum gains three, therefore three of HNO_3 are taken.

(*13*) $3BiONO_3 + 11Al + 11KOH = 3Bi + 3NH_3 + 11KAlO_2 + H_2O$

The bismuth loses three bonds and the nitrogen loses eight, therefore eleven of aluminum are taken; the aluminum gains three, therefore three of the $BiONO_3$ are taken.

(*14*) $MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$

The manganese loses two bonds and the chlorine gains one, but two more of unoxidized HCl are needed to combine with the manganese, hence four are taken.

(*15*) $2CrI_3 + 64KOH + 27Cl_2 = 2K_2CrO_4 + 6KIO_4 + 54KCl + 32H_2O$

The chromium gains three bonds and the iodine (in the molecule) gains twenty-four, therefore twenty-seven of Cl_2 are taken and the Cl_2 loses two, therefore two of CrI_3 are taken.

This rule holds good in organic chemistry when all the products of the reactions are known, as the following examples will illustrate:

CH_4	$C^{-4}H'_4$.	$-4+4=0$
CH_3Cl	$C^{-3+1}H'_3Cl^{-1}$.	$-3+1+3-1=0$
CH_2Cl_2	$C^{-2+2}H'_2Cl^{-1}{}_2$.	$-2+2+2-2=0$
$CHCl_3$	$C^{-1+3}H'Cl^{-1}{}_3$.	$-1+3+1-3=0$
CCl_4	$C^{4}Cl^{-1}{}_4$.	$4-4=0$
$HC_2H_3O_2$	$H'(C_2)^{+3-3}H'_3O^{-2}{}_2$.	$1+3-3+3-4=0$
C_2H_6O	$(C_2)^{1-5}H'_6O^{-2}$.	$1-5+6-2=0$
$C_3H_8O_3$	$(C_3)^{-5+3}H'_8O^{-2}{}_3$.	$-5+3+8-6=0$
$C_6H_{12}O_6$	$(C_6)^{-7+7}H'_{12}O^{-2}{}_6$.	$-7+7+12-12=0$

(*1*) $CH_4 + 4Cl_2 = CCl_4 + 4HCl$

The carbon is oxidized by the chlorine from negative four to positive four, a polarity change of eight units, hence take eight molecules of chlorine; each molecule of chlorine loses two bonds, take two molecules of methane. Two is to eight as one is to four.

(*2*) $3C_2H_6O + 2K_2Cr_2O_7 + 8H_2SO_4 = 3HC_2H_3O_2 + 2K_2SO_4 + 2Cr_2(SO_4)_3 + 11H_2O$

The carbon of the alcohol while possessing a valence of eight, has an oxidation valence of but four (minus four bonds); in the acetic acid the two atoms of carbon have zero bonds, that is, the combinations with negative affinity exactly equal the combinations with positive affinity; therefore take four molecules of the potassium dichromate. The two atoms of the chromium lose six bonds, take six molecules of the alcohol. Six is to four as three to two. Eight molecules of sulphuric acid are necessary to combine with the potassium and the chromium.

(*3*) $3C_3H_8O_3 + 14HNO_3 = 9CO_2 + 14NO + 19H_2O$

The three atoms of the carbon in the glycerine have minus two bonds (the negative affinity is two more than the positive affinity), and in the CO_2 a like amount has twelve bonds, a gain of fourteen. The nitrogen loses three bonds.

(*4*) $C_6H_{12}O_6 + 12H_2SO_4 = 6CO_2 + 12SO_2 + 18H_2O$

The carbon in the dextrose has zero bonds (equal positive and negative affinity combinations) and gains twenty-four bonds, while the sulphur loses two bonds. The lower ratio is one to twelve.

For convenience of reference the non-metallic elements will be described in the order of their atomic weights; and the acids in the order of the degree of oxidation of the characteristic element, *e. g.*, **N** before **S**, HCl before $HClO$, $HClO_3$ before $HClO_4$, etc.

§219. Hydrogen. H = 1.008. Valence one.

1. **Properties.**—An odorless, tasteless gas. It is the lightest body known: One litre at 0°, 760 mm. atmospheric pressure, weighs 0.08952289 gram (one crith); *specific gravity*, 0.06949 (Crafts, *C. r.*, 1888, **106**, 1662). It is used for filling balloons; also illuminating gas, containing about 50 per cent of hydrogen, is frequently used because it is much cheaper. It is a non-poisonous gas, but causes death by exclusion of air. It has been liquified to a colorless transparent liquid by cooling to —220° under great pressure and then allowing to expand rapidly (Olszewski, *C. r.*, 1884, **99**, 133; 1885, **101**, 238; Wroblewski, *C. r.*, 1885, **100**, 979). *Critical temperature*, —234.5°; *critical pressure*, 20 atmospheres; *boiling point*, —243.5° (Olszewski, *Phil. Mag.*, 1895, (5), **40**, 202). It diffuses through walls of paper, porcelain, heated platinum, iron, and other metals more than any other gas (Cailletet, *C. r.*, 1864, **58**, 327 and 1057; 1865, **60**, 344; 1868, **66**, 847). It is absorbed by charcoal and by many metals, especially palladium; which, heated to 100° in an atmosphere of hydrogen and then cooled in that atmosphere, absorbs at ordinary temperatures 982.14 volumes of hydrogen (Graham, *J. C.*, 1869, **22**, 419). This occluded hydrogen acts as a strong reducing agent, reducing $FeCl_3$ to $FeCl_2$, $HgCl_2$ to Hg^2, etc. It is a better conductor of sound than air (Bender, *B.*, 1873, **6**, 665). It conducts heat seven times better than air or 480 times poorer than iron (Stefan, *C. C.*, 1875, 529). It refracts light more powerfully than any other gas and about six times more than air. It burns with a non-luminous flame and with generation of much heat (more than an equal weight of any other substance or mixture of substances). Hydrogen forms two oxides: water, H_2O, and hydrogen peroxide, H_2O_2 (§244).

2. **Occurrence.**—In volcanic gases (Bunsen, *Pogg.*, 1851, **83**, 197). In pockets of certain Stassfurt salt crystals (Precht, *B.*, 1886, **19**, 2326). As a product of the decay of organic material, both animal and vegetable. In combination as water and in innumerable minerals (H_2O and OH) and in organic compounds.

3. **Formation.**—(*a*) By the reaction of alkali metals with water. (*b*) By the action of superheated steam upon heated metals or glowing coals (§226, 4*a*). (*c*) By dissolving aluminum or certain other metals in the fixed alkalis. (*d*) By the action of many metals with dilute acids (seldom HNO_3). By heating potassium formate or oxalate with KOH: $K_2C_2O_4 + 2KOH = 2K_2CO_3 + H_2$ (Pictet, *A. Ch.*, 1878, (5), **13**, 216).

4. **Preparation.**—(*a*) By the action of dilute sulphuric acid (one to eight) on commercial or platinized zinc * (§135, 5*a*). The solution must be kept cold or traces of SO_2 and H_2S will be evolved. (*b*) By the electrolysis of acidulated water.

5. **Solubilities.**—Water at ordinary temperature dissolves nearly two per cent (volume) of hydrogen. Charcoal dissolves or absorbs fully ten times its volume of the gas (1).

6. **Reactions.**—Hydrogen gas is a very indifferent body at ordinary temperature, combining with no other element except as it is occluded or absorbed by palladium, platinum, iron, nickel, etc.; and in the sunlight combines with chlorine and bromine. "Nascent hydrogen" (hydrogen at the moment of its generation), however, is a powerful reducing agent, and under proper

* For the rapid generation of hydrogen the zinc should be granulated by pouring the molten metal into cold water. Chemically pure zinc is very slowly attacked by dilute sulphuric acid; but the commercial zinc frequently contains sufficient impurities to insure a rapid generation of hydrogen when treated with the dilute acid. By the addition to the granulated zinc, in a tub of water, of a few cubic centimetres of a dilute solution of platinum chloride or copper sulphate, the zinc is made readily soluble in dilute sulphuric acid and a uniform and rapid generation of hydrogen can be obtained.

conditions combines with **O**, **S**, **Se**, **Te**, **Cl**, **Br**, **I**, **N**, **P**, **As**, **Sb** and **Si** with comparative readiness. The reduction of salts by nascent hydrogen in acid or alkaline solution will not be discussed here. See under the respective elements. It should be noted, however, that "nascent hydrogen" generated by different methods does not possess the same reducing properties. Sodium amalgam with acids does not give hydrogen capable of reducing silver halides; the reduction is rapid when zinc and acids are used. Neither electrolytic hydrogen nor that from sodium amalgam and acids reduces chlorates; while zinc and acids reduce rapidly to chlorides. Hydrogen generated by **KOH** and **Al** does not reduce As^{V}; that formed by zinc and acids gives AsH_3. Sb^{V} with sodium amalgam and acids gives Sb°; with zinc and acids, SbH_3 (Chabrier, *C. r.*, 1872, **75**, 484; Tommasi, *Bl.*, 1882, (2), **38**, 148).

Hydrogen occluded in metals as **Pd**, **Pt**, etc., is even more active than "nascent hydrogen"; often causing combination with explosive violence (Berthelot, *A. Ch.*, 1883, (5), **30**, 719; Berliner, *W. A.*, 1888, **35**, 781). Hydrogen absorbed by palladium precipitates **Ag**, **Au**, **Pt**, **Pd**, **Cu** and **Hg** from their solutions; permanganates acidified are reduced to Mn''; Fe''' to Fe''; Cr^{VI} to Cr'''; $KClO_3$ to $KClO$; CH_3CO_2H to CH_3CHO and C_2H_5OH; and $C_6H_5NO_2$ to $C_6H_5NH_2$. The reactions are quantitative. Salts of **Pb**, **Bi**, **Cd**, **As**, **Sb**, **W**, **Mo**, **Zn**, **Co**, **Ni**, **Al**, **Ce**, **U**, **Rb**, **Cs**, **K**, **Na**, **Ba**, **Sr** and **Ca** are not reduced (Schwarzenbach and Kritschewsky, *Z.*, 1886, **25**, 374). In the presence of platinum black hydrogen reduces very much as described above; also $K_3Fe(CN)_6$ becomes $K_4Fe(CN)_6$; dilute HNO_3 becomes NH_4NO_2, concentrated HNO_3 becomes HNO_2; **Cl**, **Br** and **I** combine with the hydrogen in the dark; $KClO_3$ and $KClO$ are reduced to chlorides. $KClO_4$ is not reduced; H_2SO_4, concentrated, is reduced to H_2SO_3 (Cooke, *C. N.*, 1888, **58**, 103).

Free hydrogen *very* slowly acts upon a neutral solution of silver nitrate, precipitating traces of silver; and in concentrated solution with formation of $AgNO_2$; hindered by HNO_3 or KNO_3. Solutions of **Au**, **Pt** and **Cu** are also acted upon (Russell, *J. C.*, 1874, **27**, 3; Leeds, *B.*, 1876, **9**, 1456; Reichardt, *Arch. Pharm.*, 1883, **221**, 585; Poleck and Thuemmel, *B.*, 1883, **16**, 2435; Senderens, *Bl.*, 1897, (3), **15**, 991). $KMnO_4$ in acid, neutral, or alkaline solution slowly oxidizes hydrogen. It is not at all oxidized by nitrohydrochloric acid, in diffused daylight, CrO_3, at ordinary temperature, $FeCl_3$, $K_3Fe(CN)_6$, HNO_3, *sp. gr.* 1.42, or H_2SO_4, *sp. gr.* 1.84 (Wanklyn and Cooper, *Phil. Mag.*, 1890, (5), **30**, 431). In some cases, when hydrogen under ordinary conditions is without action, if subjected to great pressure a reducing action takes place; *e. g.*, hydrogen at 100 atmospheres pressure precipitates Hg° from $HgCl_2$ (Loewenthal, *J. pr.*, 1860, **79**, 480).

7. **Ignition.**—Chlorine and bromine combine with hydrogen directly in the sunlight, but heat is required to effect its combination with iodine, fluorine, and oxygen.

All oxides, hydroxides, nitrates, carbonates, oxalates, and organic salts of the following elements are reduced to the metallic or elemental state by ignition in hydrogen gas: **Pb**, **Ag**, **Hg**, **Sn**, **Sb**, **As**, **Bi**, **Cu**, **Cd**, **Pd**, **Mo**, **Ru**, **Os**, **Rh**, **Ir**, **Te**, **Se**, **W**, **Fe**, **Cr**, **Co**, **Ni**, **Zn**, **Tl**, **Nb**, **In**, **V**.

Compounds of aluminum, manganese, and of the fifth and sixth group metals have not been reduced by hydrogen.

8. **Detection.**—(*a*) Method of formation if known. (*b*) Its explosive union with oxygen when the mixture with air is ignited. (*c*) Absorption by palladium sponge. (*d*) Explosive union with chlorine in the sunlight to form **HCl**. (*e*) Separated from most other gases by its non-absorption by the chemical reagents used in gas analysis.

9. **Estimation.**—By volume measurement, almost never by weight, except when determined in its compounds by combustion to H_2O.

§220. Boron. $B = 11.0$. Valence three (§2).

Boron does not occur free in nature. It is found chiefly as borax, $Na_2B_4O_7$, and as boric acid, H_3BO_3, in volcanic districts. Two varieties of the element have been prepared, amorphous and crystalline. The former is changed to the latter by heating to a white heat in presence of **Al** and **C** (Woehler and Claire-Deville, *A.*, 1867, **141**, 268). Elemental boron is prepared (*a*) by electrolysis; (*b*) by fusing B_2O_3 with **Al**, **Na** or **Mg**; (*c*) by igniting BCl_3 with hydrogen; (*d*) by fusing borax with red phosphorus. *Specific gravity* of the crystalline, 2.53 to 2.68 (Hampe, *A.*, 1876, **183**, 75); of the amorphous, 2.45. Amorphous boron is a greenish-brown, opaque powder, odorless, tasteless, insoluble in water, alcohol or ether. It is a non-conductor of electricity. Heated in air or oxygen it burns with incandescence. In air it forms B_2O_3 and **BN**. It is oxidized by molten **KOH** or $PbCrO_4$, with incandescence. It is dissolved by concentrated HNO_3 or H_2SO_4, forming boric acid. At a red heat it decomposes steam. When heated it combines directly with **S**, **Cl**, **Br**, **N** and many metals. It forms BCl_3 with chlorine, not BCl_5. Fused with P_2O_5 it forms B_2O_3 and **P**; with **KOH**, K_3BO_3 and **H**; with K_2CO_3, K_3BO_3 and **C**. Boron forms but one oxide, B_2O_3, boric anhydride. Three hydroxides are known: $2H_3BO_3 = B_2O_3.3H_2O$, orthoboric acid; $2HBO_2 = B_2O_3.H_2O$, metaboric acid; and $H_2B_4O_7 = 2B_2O_3.H_2O$, pyroboric acid.

§221. Boric acid. $H_3BO_3 = 62.024$.

$$H'_3B'''O^{-''}_3, \quad H-O-B\begin{matrix}-O-H\\-O-H\end{matrix}$$

1. **Properties.**—Boron trioxide, B_2O_3, *boric anhydride*, is a brittle vitreous mass; *sp. gr.* at 12°, 1.8476 (Ditte, *A. Ch.*, 1878, (5), **13**, 67). *Melting point*, 577° (Carnelley, *J. C.*, 1878, **33**, 278). It is volatile at a very high heat (Ebelemen, *A. Ch.*, 1848, (3), **22**, 211). It has a slightly bitter taste, is hygroscopic, and shows a marked rise in temperature on solution in water (Ditte, *C. r.*, 1877, **85**, 1069). In some respects boron trioxide deports itself as a weak base. It forms a sulphide, B_2S_3, decomposed by water (Woehler and Deville, *A. Ch.*, 1858, (3), **52**, 90); a sulphate, $B(HSO_4)_3$ (D'Arcey, *J. C.*, 1889, **55**, 155); and a phosphate, BPO_4 (Meyer, *B.*, 1889, **22**, 2919). It combines with water in three proportions, forming the ortho, meta and pyroboric acids. Orthoboric acid is a weak acid, its solutions reddening litmus; at 12° it has a *specific gravity* of 1.5172 (Ditte, *l. c.*); *melts* at 184° to 186° (Carnelley, *l. c.*). *Soluble* in 25 parts water at 20°, and in 3.4 parts at 102° (Ditte, *l. c.*). It is *volatile* in steam and in alcohol vapor. The evaporation of the water of combination of the acid carries with it from ten to fifteen per cent of the acid.

2. **Occurrence.**—Widely distributed, but usually in very small quantities. In the rock salt deposits at Stassfurt, Germany, as boracite, $Mg_7B_{16}O_{30}Cl_2$ (62.5 per cent B_2O_3). In the volcanic regions of Tuscany and the Liparic Islands as steam saturated with boric acid.

3. **Formation.**—The anhydride is formed by burning the metal in air or oxygen, or by heating the acids. Orthoboric acid, H_3BO_3, is formed by dissolving the oxide in water; the meta acid, HBO_2, $H-O-B=O$, by heating the ortho acid a little above 100° (Bloxam, *J. C.*, 1860, **12**, 177); the pyroboric acid, tetraboric acid, $H_2B_4O_7$, by heating the ortho or meta acid for some time at 160° in a current of dry air (Merz, *J. pr.*, 1866, **99**, 179).

4. **Preparation.**—(*a*) By evaporation of the water from the lagoons of Tuscany, which are saturated with boric acid, and recrystallization

from water. (*b*) The boronatrocalcite, $Ca_2B_6O_{11}.Na_2B_4O_7 + 18H_2O$ (45.6 per cent B_2O_3), found in Nevada, is evaporated in lead pans with H_2SO_4 to a stiff paste; and then treated with superheated steam in iron cylinders heated to redness. The acid passes over with the steam and is collected in lead lined chambers (Gutzkow, *Z.*, 1874, **13**, 457). (*c*) Commercial borax, $Na_2B_4O_7.10H_2O$, is dissolved in hot water, twelve parts, and acidified with hydrochloric acid. Upon cooling, the boric acid, H_3BO_3, is obtained in small scales, which are purified by recrystallization from hot water.

5. **Solubilities.**—More soluble in hydrochloric acid solution or in alcohol than in water (1). The alcoholic solution burns with a beautiful green flame. Quite soluble in glycerine and in most alcohols and hydrocarbons, only sparingly in ether. The borates are insoluble in alcohol; those of the alkalis are soluble in water to an alkaline solution. Borates of the other metals are insoluble in water (no borate is entirely insoluble in water); but are usually rendered soluble by the addition of boric acid.

6. **Reactions.**—**Silver nitrate** forms, in solutions of acid borates, a white precipitate *of silver metaborate,* $AgBO_2$, but normal borates form in part silver oxide, brown. **Lead acetate** gives a white precipitate of *lead metaborate,* $Pb(BO_2)_2$; **calcium chloride,** in solutions not very dilute, a white precipitate of *calcium metaborate;* and **barium chloride,** in solutions not dilute, a white precipitate of *barium metaborate,* $Ba(BO_2)_2$. With **aluminum** salts, the precipitate is *aluminum hydroxide.*

Borates are transposed with formation of boric acid, by all ordinary acids—in some conditions even by carbonic acid.

The liberated boric acid is dissolved by **alcohol,** and if the alcohol solution be set on fire, it burns with a *green flame.*

A solution of a borate, acidulated with hydrochloric acid to a barely perceptible acid reaction, imparts to a slip of **turmeric paper** half wet with it, a dark-red color, which on drying intensifies to a characteristic *red color* which turns dark green when moistened with a drop of alkali.

7. **Ignition.**—Boric acid is displaced from its salts by nearly all acids including CO_2; but being non-volatile except at a very high heat, it displaces most other acids upon ignition.

By heating a mixture of borax, acid sulphate of potassium, and a fluoride, fused to a bead on the loop of platinum wire, in the clear flame of the Bunsen gas-lamp, an evanescent yellowish-green color is imparted to the flame.

Borates fused in the *inner blow-pipe flame* with potassium acid sulphate give *the green color* to the outer flame.

If a crystal of boric acid, or a solid residue of borate previously treated with sulphuric acid, on a porcelain surface, is played upon by the flame of Bunsen's Burner, the green flame of boron is obtained.

If a powdered borate (previously calcined), is moistened with sulphuric acid and heated on platinum wire to expel the acid, then moistened with **glycerine** and burned, the green flame appears with great distinctness. The glycerine is only ignited, then allowed to burn by itself. Barium does not interfere (being held as sulphate, non-volatile); copper should be previously removed in the wet way. The glycerine flame gives the spectrum. But in all flame tests, the boric acid must be liberated.

Borates (fused on platinum wire with sodium carbonate) give a characteristic spectrum of four lines, equidistant from each other, and extending from **Ba** γ in the green to **Sr** δ in the blue.

Borax, $Na_2B_4O_7$, when ignited (as on a loop of platinum wire to form the borax bead) with many metallic compounds, forms a colored glass, used in the detection of certain metals (§**132**, 7). The fused borax forms a solid brittle mass, borax glass, used in assaying and in soldering because of its power of combination with metallic oxides.

8. **Detection.**—By conversion into the acid, if present as a salt; solution in alcohol or glycerine and burning with the formation of the green flame (very delicate, but copper salts should be removed by H_2S and barium salts should be removed or converted into the sulphate). Also by the red color imparted to a strip of turmeric paper.

9. **Estimation.**—Boron compounds cannot be completely precipitated from solution by any known reagents, hence most of the methods of quantitative determination are indirect. By adding a known quantity of Na_2CO_3, fusing and weighing; then after determining the CO_2 subtracting its weight and that of the Na_2O present (calculated from Na_2CO_3 first added). The difference is the weight of B_2O_3 present. See also Will (*Arch. Pharm.*, 1887, **225**, 1101). In the presence of glycerine or mannitol, boric acid may be accurately titrated with sodium hydroxide, using phenolphthalein as an indicator: $B_2O_3 + 2NaOH = 2NaBO_2 + H_2O$. Sodium carbonate must be absent or we get: $2B_2O_3 + Na_2CO_3 = Na_2B_4O_7 + CO_2$ (Honig and Spitz, *Z. angew.*, 1896, 549; Joergensen, *Z. angew.*, 1897, 5).

§222. Carbon. C = 12.0. Usual valence four (§15).

1. **Properties.**—Carbon exists in three allotropic forms: two crystalline, diamond and graphite, and amorphous as charcoal, coke, etc. *Specific gravity*, diamond at 4°, 3.51835 (Baumhauer, *J.*, 1873, 237); graphite, Ceylon, 2.25 to 2.26 (Brodie, *A.*, 1860, **114**, 6); wood charcoal, 1.57; gas coke, 1.88. Very small specimens only, of diamonds have been artificially prepared, by saturating iron with carbon at 3000°. At this temperature graphite is formed and upon cooling under pressure the crystalline diamond form is obtained. This cooling under pressure is obtained by pouring the carbon saturated iron into a soft iron bomb, which is cooled by water (Moisson, *C. r.*, 1893, **116**, 218). Diamond is the hardest substance known. It is very strongly refractive towards light (Becquerel, *A. Ch.*, 1877, (5), **12**, 5). Fluorescence and phosphorescence of diamonds, see Kunz (*C. C.*, 1891, **ii**, 562). Ignition in an atmosphere of hydrogen does not effect a change; in air or oxygen it burns to CO_2.

Graphite is a hard, gray, metal-like, opaque solid, a good conductor of electricity and a fairly good conductor of heat. It burns with difficulty. It

is used in lead pencils, in black lead (plumbago) crucibles, as a lubricant for heavy machinery, in battery plates, for the arc light carbon pencils, etc.

Amorphous carbon is black, lighter than diamond or graphite. It is in use as coal, coke, charcoal, animal charcoal, etc.; all impure forms. Lamp-black is also amorphous carbon made from burning resin, fat, wax, coal gas, etc., with limited supply of air. It is used as a pigment in paints, in stove-blacking, shoe-blacking, printers' ink, etc. Charcoal, preferably animal charcoal, is used for decoloring organic solutions. Charcoal absorbs many gases, hence is valuable as a disinfectant.

Carbon forms two oxides: carbon monoxide, **CO**, and carbon dioxide, CO_2.

2. **Occurrence.**—Diamonds seem first to have been found in India, especially in the Golconda pits, where, as early as 1622, 30,000 laborers are said to have been employed (Walker, *J.*, 1884, 774). Also found in other parts of Asia, in South Africa, in Brazil, etc. (Winklehner, *C. C.*, 1888, 192; Damour, *J.*, 1883, 774; Gorceix, *J.*, 1881, 345; Smit, *J.*, 1880, 1400). Graphite is found in Ceylon (Walther, *C. C.*, 1890, **ii**, 20); in California (*C. N.*, 1868, **17**, 209); in Canada (Dawson, *Am. S.*, 1870, (2), **50**, 130); in New York State; in New Zealand (Mac Ivor, *C. N.*, 1887, **55**, 125); in Russia, Germany, Greenland, etc. Pure amorphous carbon occurs in nature as a chief product in the decomposition of organic material, air being excluded. Anthracite coal is relatively pure amorphous carbon.

3. **Formation.**—Graphite remains as a residue when pig iron is dissolved in acids. It forms by reducing **CO** with Fe_3O_4 at 400°. Amorphous carbon is formed by passing CCl_4 over **Na** in a tube heated to redness (Porcher, *C. N.*, 1881, **44**, 203).

4. **Preparation.**—Pure graphite is prepared by heating the commercial graphite on a water bath with $KClO_3$ and H_2SO_4 and repeatedly washing. If it contains SiO_2 it should also be treated with **NaF** and H_2SO_4. Amorphous carbon is prepared by heating wood, coal, or almost any organic matter to a very high temperature in absence of air, but when so prepared it is never pure. Amorphous carbon is prepared approximately pure by heating pure cane sugar in a closed platinum crucible; then boiling in succession with **HCl**, **KOH**, and H_2O; then igniting to redness in an atmosphere of chlorine, cooling in the same atmosphere. A very pure form of graphite known as Acheson graphite is made in large quantities at Niagara Falls by passing a strong electric current through coke compressed into the desired form. Silicon, aluminum and other impurities are distilled out at the high temperature employed.

5. **Solubilities.**—Insoluble in water or acids. Soluble in many molten metals with partial combination to form carbides. When the metal is dissolved in acids the combined carbon passes off as hydrocarbons, the excess remaining as graphite.

6. **Reactions.**—Not attacked by acids or alkalis. It slowly oxidizes to CO_2 when heated with concentrated H_2SO_4 and $K_2Cr_2O_7$. Upon gently warming graphite with $KClO_3$ and HNO_3, graphitic acid, $C_{11}H_4O_6$, is said to be formed (Stingl, *B.*, 1873, **6**, 391). The important reactions of carbon require the aid of high heat and are described in the next paragraph.

7. **Ignition.**—Unchanged by ignition in absence of air. When strongly ignited in air or oxygen it slowly burns to CO_2. If the carbon and oxygen has been previously very thoroughly dried the action is very slow, especially with graphite. By fusion with KNO_3 or $KClO_3$ carbon is oxidized to CO_2. With vapors of sulphur, carbon disulphide is formed; *i. e.*, by passing sulphur vapors over hot coals in an electrically heated furnace. In an atmosphere of hydrogen with the electric spark, acetylene, C_2H_2, is formed. By igniting in an atmosphere of carbon dioxide, CO_2, the whole of the carbon becomes carbon monoxide: $C + CO_2 = 2CO$.

By simple ignition with carbon, all oxides of the elements in the following list are reduced to the elemental state (*a*); and if sodium carbonate is added, all of the salts of the same are likewise reduced (*b*). **Cu**, **Bi**, **Cd**, **Pb**, **Ag**, **Hg**, **As**, **Sb**, **Sn**, **Pd**, **Mo**, **Ru**, **Os**, **Rh**, **Ir**, **Te**, **Se**, **W**, **K**, **Na**, **Rb**, **Cr**, **Fe**, **Mn**, **Co**, **Ni**, **Zn**, **Ti**, **Tl**.

(*a*) $Pb_3O_4 + 2C = 3Pb + 2CO_2$
(*b*) $2PbCl_2 + 2Na_2CO_3 + C = 2Pb + 4NaCl + 3CO_2$
(*c*) $CuO + C$ (excess) $= Cu + CO$
(*d*) $C + 2CuO$ (excess) $= 2Cu + CO_2$

With excess of carbon **CO** is formed (*c*). With excess of the oxide CO_2 is formed (*d*). In the reduction of iron ore, the process is conducted so as to give some **CO** and some CO_2. To obtain some metals in the free state (such as **K** and **Na**), special methods are adopted to exclude the air, and to produce the high temperature needed.

All compounds of sulphur when ignited with carbon are reduced to a sulphide: $BaSO_4 + 2C = BaS + 2CO_2$.

8. **Detection.**—By its appearance; failure to react with general reagents; and by its combustion to CO_2 with oxygen (air), or with $K_2Cr_2O_7$ and concentrated H_2SO_4 (Fritsche, A., 1896, **294**, 79), then by identification with $Ca(OH)_2$ (§228, 6).

9. **Estimation.**—By combustion to CO_2 and weighing after absorption in **KOH** solution. See works on ultimate organic analysis.

§223. Acetic acid. $HC_2H_3O_2 = 60.032$.

$$H'_4(C_2)^{+'''-'''}O^{-''}{}_2, \quad H-\underset{H}{\overset{H}{C}}-\overset{O}{\overset{\|}{C}}-O-H = CH_3CO_2H.$$

1. **Properties.**—Pure acetic acid is a colorless, crystalline, hygroscopic solid, melting at 16.5° and boiling at 118°. Its *specific gravity* at 0° is 1.080. It has a sharp, sour taste, an irritating burning effect on the skin, and a very pene-

trating odor. It burns when heated nearly to the boiling point. Vinegar contains four to five per cent of acetic acid. The U. S. P. reagent contains 36 per cent of acetic acid, and has a specific gravity of 1.0481 at 15°. It vaporizes from its concentrated solutions at ordinary temperature, having the characteristic odor of vinegar. It is a monobasic acid, as the three remaining hydrogen atoms (linked to carbon) cannot be replaced by metals.

2. **Occurrence.**—It occurs in nature in combination with alcohols in the essential oils of many plants.

3. **Formation.**—(*a*) During the decay of many organic compounds. (*b*) By gently heating sodium methylate, $NaOCH_3$, in a current of carbon monoxide: $NaOCH_3 + CO = CH_3CO_2Na$ ($NaC_2H_3O_2$). (*c*) By boiling methyl cyanide with acids or alkalis: $CH_3CN + HCl + 2H_2O = HC_2H_3O_2 + NH_4Cl$. (*d*) By the oxidation of alcohol: $3C_2H_6O + 2K_2Cr_2O_7 + 8H_2SO_4 = 2K_2SO_4 + 2Cr_2(SO_4)_3 + 3HC_2H_3O_2 + 11H_2O$.

4. **Preparation.**—(*a*) By the dry distillation of wood. (*b*) By the fermentation of cider, beer, wine, molasses, etc. (*c*) Pure acetic acid is prepared by distilling anhydrous sodium acetate with concentrated sulphuric acid. The distillate solidifies upon cooling and is termed glacial acetic acid.

5. **Solubilities.**—Miscible in all proportions in water and alcohol. The salts of acetic acid, acetates, are all soluble in water, silver and mercurous acetates sparingly soluble. One part of silver acetate requires 115 parts of water at 10° for its solution; one part of mercurous acetate requires 300 parts of water. Certain *basic* acetates, as Fe''', Al, etc., are insoluble in water. Very many of the acetates are soluble in alcohol. Ammonium acetate dissolves several insoluble sulphates such as calcium and lead sulphates.

6. **Reactions.**—The stronger mineral acids transpose the acetates, forming acetic acid. Anhydrous acetates with concentrated sulphuric acid give pure acetic acid (4), but if the sulphuric acid be in excess and heat be applied the mixture blackens with separation of carbon; and, at higher temperatures, CO_2 and SO_2 are evolved.

Solution of **ferric chloride** forms, with solutions of acetates, a *red solution* containing *ferric acetate*, $Fe(C_2H_3O_2)_3$, which on boiling precipitates brownish-red, basic ferric acetate. The red solution is not decolored by solution of mercuric chloride (distinction from thiocyanate); but is decolored by strong acidulation with sulphuric acid or hydrochloric acid (distinction from thiocyanate and from meconate). The ferric acetate is precipitated by alkali hydroxides.

If acetic acid or an acetate be warmed with **sulphuric acid** and a *little* **alcohol**, the characteristic pungent and *fragrant odor of ethyl acetate* or acetic ether is obtained:

$$HC_2H_3O_2 + C_2H_5OH = H_2O + C_2H_5C_2H_3O_2$$

Acetic acid does not act as a **Reducing Agent** as readily as do most of

the organic carbon compounds. Acetic acid is stable toward mild oxidizing agents and is only slowly attacked by strong oxidizing agents such as chromic acid and potassium permanganate; reduces auric chloride only in alkaline solution, and does not reduce alkaline copper solution. It takes chlorine into combination—slowly in ordinary light, quickly in sunlight, forming chloracetic acids.

Acetic acid is a weak acid, only 0.4% being ionized in normal solution and 1.4% in tenth normal solution. Glacial acetic acid dissolves sulphur which crystallizes out in needles.

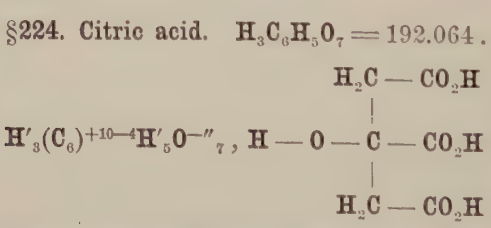
7. **Ignition.**—By **ignition** alone, acetates blacken, with evolution of vapor of *acetone*, C_3H_6O, inflammable and of an agreeable odor. By prolonged ignition of alkali acetates in the air, carbonates are obtained free from charcoal. By ignition with **alkali hydroxides** in dry mixtures, methane, *marsh-gas*, CH_4, is evolved. By ignition with **alkalis** and **arsenous anhydride**, the poisonous and offensive vapor of cacodyl oxide is obtained. This test should be made under a hood with great caution and with small quantities. It is a very delicate test for acetates: $4KC_2H_3O_2 + As_2O_3 = As_2(CH_3)_4O + 2K_2CO_3 + 2CO_2$.

Butyric, propionic and valerianic acids give the same reaction.

8. **Detection.**—(*a*) By its odor. (*b*) By the formation of the fragrant ethyl acetate upon warming with sulphuric acid and alcohol. Too much alcohol should not be used in testing for acetic acid as otherwise ethyl ether is formed. (*c*) By the formation of the red solution with ferric chloride (§126, 6b and §152). (*d*) By ignition of the dry acetate alone to acetone, CH_3COCH_3; with **NaOH** to methane, CH_4; or with As_2O_3 to cacodyl oxide. (*e*) As a delicate test for formates or acetates it is directed to warm a solution of $CuCl_2$ in **NaCl** and add a small amount of the material under examination. Formates give a blackish-gray deposit; acetates give a bright green precipitate not changed by boiling. Both precipitates are soluble in acetic acid (Field, *J. C.*, 1873, **26**, 575).

9. **Estimation.**—Other volatile acids are separated by precipitation; sulphuric acid is then added and the acetic acid is distilled into water and estimated by titration with standard alkali.

§224. **Citric acid.** $H_3C_6H_5O_7 = 192.064$.



Found in small quantities in the juices of many fruits. The chief commercial source is lemon-juice. It is a colorless, crystallizable, non-volatile solid; it is

soluble in 0.75 parts of cold water, in equal parts of 90 per cent alcohol, in 1.3 parts of absolute alcohol and in 50 parts of ether. It crystallizes with one molecule of water in rhombic prisms which melt at 100°.

The **citrates** of the metals of the alkalis are freely **soluble in water;** those of iron and copper are moderately soluble; those of the alkaline earth metals insoluble. There are many soluble double citrates formed by action of alkali citrates upon precipitated citrates, or of alkali hydroxides upon metallic salts in presence of citric acid. In **distinction** from tartrates, the solubility of the potassium salts, non-precipitation of calcium salt in cold solution; and weaker reducing action, are to be noted.

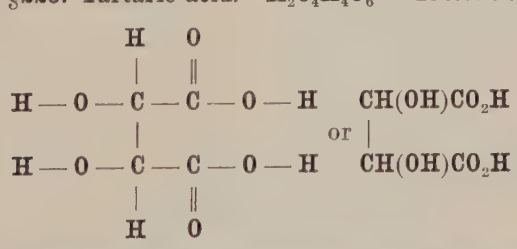
Solution of **calcium hydroxide** in excess (as by dropping the solution tested into the reagent) gives no precipitate with citric acid or citrates in the cold (distinction from tartaric acid), but on heating, the white *calcium citrate*, $Ca_3(C_6H_5O_7)_2$, is precipitated (not soluble in cold potassium hydroxide solution). By filtering before boiling, the tartrate and citrate may be approximately separated. The chlorides of calcium and barium give no precipitate in neutral solutions (difference from tartaric acid), but if sodium hydroxide is added, calcium citrate is precipitated, insoluble in sodium hydroxide, but readily soluble in ammonium chloride. On boiling the solution in ammonium chloride, crystallized calcium tartrate is precipitated, which is now insoluble in ammonium chloride. Calcium citrate is soluble in acetic acid (distinction from oxalates).

Solution of **lead acetate** precipitates white *lead citrate*, $Pb_3(C_6H_5O_7)_2$, soluble in ammonia. **Silver nitrate** gives a white precipitate of *silver citrate*, $Ag_3C_6H_5O_7$, which does not blacken on boiling (distinction from tartrate). For action of citric acid or citrates in hindering many of the usual analytical reactions, see Spiller, *J. C.*, 1858, **10**, 110.

One part of citric acid dissolved in two parts of water, and treated with a solution of one part of potassium acetate in two parts of water, should remain clear *after* addition of an equal volume of strong alcohol (absence of oxalic acid and of tartaric acid and its isomers).

Citric acid does not act very readily as a **reducing agent;** does not reduce alkaline copper solution, or silver solution; reduces permanganate very slowly. Concentrated nitric acid produces from it, acetic and oxalic acids; and digestion with manganese dioxide decomposes it with formation of acetone, acrylic and acetic acids. Concentrated sulphuric acid carbonizes citric acid with liberation of sulphur dioxide. Citrates carbonize on **ignition,** with various empyreumatic products, and with final formation of carbonates. On heating citric acid, it loses its water of crystallization, then fuses and decomposes with evolution of pungent fumes leaving a carbonaceous residue. By fused potassium hydroxide, short of ignition, they are decomposed with production of oxalate and acetate.

§225. Tartaric acid. $H_2C_4H_4O_6 = 150.048$.



1. **Properties.**—Tartaric acid is a colorless, crystalline, non-volatile solid; soluble in 0.756 parts of water at 15°, in 3.4 parts of 90 per cent alcohol, in 50 parts of ordinary ether and 250 parts of absolute ether. It exists in four distinct modifications: dextrotartaric acid, levotartaric acid, racemic acid, and mesotartaric acid. They differ from each other in crystalline form, in solubility,

and especially in the deportment of their solutions towards polarized light. Racemic and mesotartaric acids are optically inactive, but the former may be resolved into the first two acids, optically active.

2. **Occurrence.**—It is found in various fruits. The chief commercial source is grape juice.

3. **Formation.**—By oxidation of dextrose, cane sugar, milk sugar, starch, etc., with HNO_3 (Kiliani, *A.*, 1880, **205**, 175). By action of sodium amalgam on oxalic ether in alcoholic solution (Debus, *A.*, 1873, **166**, 124). By synthesis from succinic acid by formation first of the dibromsuccinic acid, $H_2C_4Br_2H_2O_4$; then substitution of the **OH** group for the bromine by means of water and silver oxide.

4. **Preparation.**—The crude argol deposited during the fermentation of grape juice is recrystallized, giving the commercial cream of tartar, $KHC_4H_4O_6$. This in hot solution is treated with powdered chalk, and the filtrate from the precipitate thus obtained is precipitated with calcium chloride. Both precipitates are washed and decomposed by the necessary quantity of hot dilute sulphuric acid. The tartaric acid solution is evaporated to crystallization and purified by recrystallization (Ficinius, *Arch. Pharm.*, 1879, **215**, 14 and 310).

5. **Solubilities.**—The **Tartrates** of the alkali bases are **soluble in water**; the normal tartrates being freely soluble, the acid tartrates of potassium and ammonium sparingly soluble. The tartrates of the alkaline earth bases and of the non-alkaline bases, are insoluble or sparingly soluble, but mostly dissolve in solution of tartaric acid. Most of the tartrates are insoluble in alcohol. There are double tartrates of heavy metals with alkali metals, which dissolve in water. Tartar-emetic is potassium antimonyl tartrate, $KSbOC_4H_4O_6$.

Hydrochloric, nitric, and sulphuric **acids** transpose the tartrates (whether forming solutions or not). Most of the tartrates are also dissolved (and, if already dissolved, are not precipitated) by the **alkali hydroxides,** owing to the formation of soluble double tartrates.

The freshly precipitated oxides, hydroxides, and carbonates of the following metals are soluble in a solution of potassium-sodium tartrate, *Rochelle salt:* **Sb**, Sn^{IV}, **Bi**, **Cu**, **Fe**, **Al**, **Cr**, **Co**, **Ni**, **Mn**, and **Zn**; **Ba**, **Sr**, **Ca**, and **Mg** to quite an extent. $CdCO_3$ is not dissolved (Warren, *C. N.*, 1888, **57**, 223).

6. **Reactions.**—Solution of **calcium hydroxide**, added to alkaline reaction, precipitates from cold solution of tartaric acid, or of soluble tartrates, *calcium tartrate*, white, $CaC_4H_4O_6$. Solution of calcium chloride with neutral tartrates gives the same precipitate. Solution of calcium sulphate forms a precipitate but slowly, or not at all (distinction from racemic acid). The precipitate of calcium tartrate is soluble in cold solution of potassium hydroxide, precipitated gelatinous on boiling, and again made soluble on cooling (distinctions from citrate), and dissolves in acetic acid (distinction from oxalate).

Tartaric acid prevents the precipitation by fixed alkalis of solutions of the salts of the following metals: **Al**, **Bi**, **Co**, **Ni**, **Cr**, **Cu**, **Fe**, **Pb**, **Pt**, and **Zn** (Grothe, *J. pr.*, 1864, **92**, 175).

Silver nitrate precipitates, from solutions of normal tartrates, *silver tartrate*, $Ag_2C_4H_4O_6$, white, becoming black when boiled. If the precipitate is filtered, washed, dissolved from the filter by dilute ammonium hydroxide into a clean test-tube, left for a quarter of an hour on the water-bath, the silver is reduced as a *mirror coating* on the glass (§**59**, 10b), distinction from citric acid. Free tartaric acid does not reduce silver salts. **Permanganate** is **reduced** quickly by alkaline solution of tartrates (distinction from citrates), precipitating manganese dioxide, brown. Free tartaric acid acts but slowly on the permanganate. Alkaline copper tartrate, Fehling's solution (§**77**, 6b), resists reduction in boiling solution. **Chromates** are reduced by tartaric acid, the solution turning green. The oxidized products, both with permanganate and chromate, are formic acid, carbonic anhydride, and water.

7. **Ignition.**—On **ignition**, tartaric acid or tartrates evolve the *odor of burnt sugar, separating carbon*, and becoming finally converted to carbonates.—Strong **sulphuric acid** also blackens tartrates, on warming. Melted **potassium hydroxide**, below ignition, produces acetate and oxalate. The fixed alkali tartrates ignited in absence of air give an alkali carbonate and finely divided carbon. The mixture serves as an admirable flux for the reduction tests for arsenic (§**69**, 7).

8. **Detection.**—(*a*) By the odor of burnt sugar when ignited. (*b*) By the deportment of the calcium salt with cold and hot **KOH** (6). (*c*) By the formation of the silver mirror (§**59**, 10b). (*d*) By its action as an alkali tartrate in preventing precipitation of the solutions of the heavy metals by the fixed alkalis. To test citric acid for the presence of tartaric acid, add about one cc. of ammonium molybdate solution to about one gram of the citric acid; then two or three drops of sulphuric acid and warm on the water-bath. The presence of 0.1 per cent or more of tartaric acid gives a blue color to the solution (Crismer, *Bl.*, 1891, (3), **6**, 23). Add to tartaric acid or a tartrate a little ferrous sulphate, then one to two drops of hydrogen peroxide, then alkali—the presence of tartaric acid will be indicated by a deep violet color (Fenton, Chem. News, 43, 110). Heat tartaric acid with a little resorcin and concentrated sulphuric acid in a porcelain dish to 125-130° C. First, red streaks will appear, then the whole liquid turns red. Sensitiveness 0.01 mg. tartaric acid (Mohler, Bull. Soc. Chim. France [3], 4, 1890, 728). This reaction depends upon the formation of an aldehyde and its subsequent condensation with resorcin.

The test can be used to distinguish between citric and tartaric acids. If α-naphthol is used in place of resorcin, a blue liquid turning green is the result (Piñeaúa, *Chem. News*, 91, 179).

9. **Estimation.**—See Philipps (*Z.*, 1890, **29**, 577); Haas (*C. C.*, 1888, 1045); Heidenhain (*Z.*, 1888, **27**, 681).

§226. Carbon monoxide. $CO = 28.0$.

$C''O^{-''}$, $C = O$.

1. **Properties.**—*Carbon monoxide, carbonic oxide, formic anhydride*, **CO**, is a colorless, tasteless gas. *Specific gravity*, 0.9678. By maintaining a pressure of 200 to 300 atmospheres at —136° and then reducing the pressure to 50 atmospheres the gas becomes a colorless transparent liquid (Wroblewski and Olszewski, *A. Ch.*, 1884 (6), **1**, 128). It is, when inhaled, a virulent poison, abstracting oxygen from the blood and combining with the haemoglobin. It burns in the air with a pale blue flame to CO_2, but does not support combustion. Mixed with air in suitable proportions, it explodes upon ignition. It unites with chlorine in the sunlight to form phosgene, $COCl_2$.

2. **Occurrence.**—In combination as formic acid in ants and in nettles.

3. **Formation.**—(*a*) By the incomplete combustion of coal, charcoal or organic material. (*b*) From the reduction of metallic oxides in the blast furnace with excess of charcoal: $Fe_2O_3 + 3C = 2Fe + 3CO$. (*c*) By heating sodium sulphate with excess of charcoal (LeBlanc's soda process): $Na_2SO_4 + 4C = Na_2S + 4CO$. See also Grimm and Ramdohr (*A.*, 1856, **98**, 127).

4. **Preparation.**—(*a*) By passing steam over charcoal at a white heat (water gas): $H_2O + C = CO + H_2$ (Naumann and Pistor, *B.*, 1885, **18**, 164). (*b*) By passing CO_2 over red hot charcoal. (*c*) By heating $K_4Fe(CN)_6$ with concentrated H_2SO_4: $K_4Fe(CN)_6 + 6H_2SO_4 + 6H_2O = 2K_2SO_4 + 3(NH_4)_2SO_4 + FeSO_4 + 6CO$. With dilute acid **HCN** is formed. (*d*) By heating a formate with concentrated sulphuric acid: $2KCHO_2 + H_2SO_4 = K_2SO_4 + 2CO + 2H_2O$. (*e*) By heating an oxalate with concentrated sulphuric acid: $K_2C_2O_4 + 2H_2SO_4 = K_2SO_4 + H_2SO_4.H_2O + CO + CO_2$.

5. **Solubilities.**—It is not absorbed by **KOH** or $Ca(OH)_2$ (distinction from CO_2). It is absorbed by charcoal, cuprous chloride, and by several metals, *e. g.*, **K**, **Ag**, and **Au**.

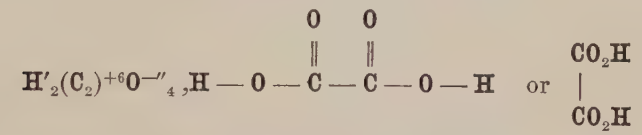
6. **Reactions.**—It is an energetic reducing agent. Combines with moist fixed alkalis to form a formate (Froelich and Geuther, *A.*, 1880, **202**, 317). In the sunlight it combines directly with chlorine or bromine. It is oxidized to CO_2 by warming with $K_2Cr_2O_7$ and concentrated H_2SO_4; also by palladium sponge saturated with hydrogen, and in presence of oxygen and water (Remsen and Keiser, *B.*, 1884, **17**, 83). A solution of $PdCl_2$ is reduced to **Pd** by **CO**. Reduces iodine pentoxide I_2O_5 at 150°, $I_2O_5 + 5CO = I_2 + 5CO_2$.

7. **Ignition.**—When heated to redness with **Na** or **K**, carbon and an alkali carbonate are formed. Upon ignition of metallic oxides in an atmosphere of **CO** a reduction of the metal takes place, so far as observed the same as when the corresponding metallic forms are ignited with charcoal (Rodwell, *J. C.*, 1863, **16**, 44).

8. **Detection.**—In distinction from CO_2 by its failure to be absorbed by **KOH** or $Ca(OH)_2$. By its combustion to CO_2 and detection as such. By its combination with hot concentrated **KOH** to form a formate. By its action on I_2O_5. It is detected in the blood by the absorption spectrum (Vogel, *B.*, 1878, **11**, 235).

9. **Estimation.**—The measured volume of the gas is brought in contact with a solution of cuprous chloride in hydrochloric acid which absorbs the **CO** (Thomas, *C. N.*, 1878, **37**, 6). The gas is passed through a U-tube containing I_2O_5 heated to 150°. The liberated iodine is absorbed in **KI** solution and titrated with standard $Na_2S_2O_3$ solution. *Jour. Am. Chem. Soc.*, 1900, **22**, 14.

§227. Oxalic acid. $H_2C_2O_4 = 90.016$.



1. **Properties.**—Absolute oxalic acid, $H_2C_2O_4$, is a white, amorphous solid, which may be sublimed at 150° with only partial decomposition: $H_2C_2O_4 = CO_2 + CO + H_2O$. Crystallized oxalic acid, $H_2C_2O_4,2H_2O$, effloresces very slowly in warm, dry air, and melts in its water of crystallization at 98°; at which temperature the liquid soon evaporates to the absolute acid. Oxalic anhydride is not formed.

2. **Occurrence.**—Found in many plants in a free state or as an oxalate. In sorrel it is found as KHC_2O_4; in rhubarb as CaC_2O_4. As ferrous oxalate in lignite deposits; as ammonium oxalate in guano.

3. **Formation.**—(*a*) By decomposition of cyanogen with water, ammonium oxalate being one of the products. (*b*) By the oxidation of glycol with nitric acid. (*c*) By heating potassium formate above 400° (Merz and Weith, *B.*, 1882, **15**, 1507). (*d*) By passing CO_2 over a mixture of sodium and sand at 360° (Drechsel, *Bl.*, 1868, **10**, 121).

4. **Preparation.**—(*a*) By action of nitric acid sp. gr. 1.38 upon sawdust, starch, or sugar. By the continued action of concentrated nitric acid, after the sugar is all oxidized to oxalic acid, the latter is farther oxidized to CO_2. (*b*) By heating sawdust with **KOH** or **NaOH**. Hydrogen is evolved, the cellulose, $C_6H_{10}O_5$, being converted into oxalic acid. Under certain conditions, additional products are formed. It is also formed in the oxidation of a great many organic compounds.

$$C_{12}H_{22}O_{11} + 12HNO_3 = 6H_2C_2O_4 + 12NO + 11H_2O$$
$$3H_2C_2O_4 + 2HNO_3 = 6CO_2 + 2NO + 4H_2O$$
$$C_6H_{10}O_5 + 6KOH + H_2O = 3K_2C_2O_4 + 9H_2$$

Oxalates are formed: *a*.—By treating the oxide, hydroxide, or carbonate with oxalic acid. In this manner may be made the oxalates of

Pb, **Ag**, **Hg′**, **Hg″**, **Sn″**, **Bi**, **Cu″**, **Cd**, **Zn**, **Al**, **Co**, **Ni**, **Mn**, **Fe″**, **Fe‴**, **Cr‴**, **Ba**, **Sr**, **Ca**, **Mg**, **Na**, **K**, and some others.

b.—By adding oxalic acid to some soluble salt of the metal. In this manner the above oxalates may be made, except alkali, magnesium, chromic, ferric, aluminum and stannic oxalates, which are not precipitated. Antimonous salts are precipitated, but the precipitate is basic.

c.—Alkali oxalates will precipitate the same solutions as oxalic acid, but many of the precipitates are soluble in excess of the alkali oxalate, and, as a rule, the salt formed is a double one, *e. g.*, $AgNH_4C_2O_4$. **Ba**, **Ca** and **Sr** are well-defined exceptions to this rule—their precipitates, formed by this method, being normal oxalates.

d.—Some of the metals when finally divided are attacked by oxalic acid, hydrogen being evolved.

5. **Solubilities.**—Oxalic acid is very soluble in water and in alcohol. Alkali oxalates are freely soluble in water, as is also chromic oxalate. Nearly all other metallic oxalates are insoluble in water or only sparingly soluble (Luckow, *J. C.*, 1887, **52**, 529).

The metallic oxalates, soluble and insoluble, are transposed by **dilute sulphuric, hydrochloric,** and **nitric** acids, with formation of *oxalic acid:* $CaC_2O_4 + 2HCl = CaCl_2 + H_2C_2O_4$. That is: the precipitated oxalates of those metals, which form soluble chlorides, *dissolve in dilute hydrochloric acid;* of those metals which form soluble sulphates, in dilute sulphuric acid; and all precipitated oxalates dissolve in dilute nitric acid

Acetic acid does not dissolve precipitated oxalates, or but slightly. Certain of the oxalates dissolve, to some extent, in **oxalic acid** (as acid oxalates).

6. **Reactions.**—*A.*—**With metals and their compounds.**—Oxalic acid and soluble oxalates precipitate solutions of many of the metallic salts. With excess of the alkali oxalates soluble double oxalates of the heavy metals are frequently formed (4). An excess of alkali oxalate transposes partially the alkaline earth carbonates. On the other hand, the alkali carbonates in excess partially transpose the alkaline earth oxalates (Smith, *J. C.*, 1877, **32**, 245). See also under 6*b* of the respective metals.

Oxalic acid is a decided **reducing agent**, being converted to *water and carbonic anhydride* (*a*), and the metallic oxalates to *carbonates and carbonic anhydride* (*b*), by all strong oxidizing agents.

$$(a)\quad 2H_2C_2O_4 + O_2 = 2H_2O + 4CO_2$$
$$(b)\quad 2K_2C_2O_4 + O_2 = 2K_2CO_3 + 2CO_2$$

1.—PbO_2 with oxalic acid forms lead oxalate and CO_2. Oxalic acid has no action upon Pb_3O_4, but reduces it quickly in presence of any acid capable of changing the Pb_3O_4 to PbO_2.

2. Oxalic acid or ammonium oxalate boiled in the sunlight with $HgCl_2$ gives **HgCl** and CO_2 [*Gmelin's Hand-book*, **9**, 118].

3.—H_3AsO_4 becomes H_3AsO_3, and CO_2 is evolved. To prove that As^V becomes As''', add excess of potassium hydroxide, and then potassium permanganate. The latter will be quickly decolored.

4.—Bi_2O_5 becomes bismuth oxalate and CO_2.

5.—Mn''^{+n} becomes Mn''. (That is, all compounds of manganese having more than two bonds are reduced to the dyad.) In absence of other free acid, MnC_2O_4 is formed, and CO_2 is given off. If some non-reducing acid be present, such as H_2SO_4, it unites with the manganese, and all of the oxalic acid is converted into CO_2.

6.—Co_2O_3 and $Co(OH)_3$ form cobaltous oxalate, and CO_2 is evolved.

7.—Ni_2O_3 and $Ni(OH)_3$ become nickelous oxalate, and CO_2 is evolved.

8.—H_2CrO_4 is reduced to chromic oxalate, and CO_2 is evolved.

As a rule, reducing agents have no action on oxalic acid at ordinary temperatures. By fusion, however, a few metals, **K**, **Na**, **Mg**, etc., reduce it to free carbon.

B.—**With non-metals and their compounds.**

1.—**HCN**, **HCNS**, $H_4Fe(CN)_6$, and $H_3Fe(CN)_6$ seem to be without action upon oxalic acid.

2.—HNO_2 seems to have no action upon $H_2C_2O_4$. With HNO_3, CO_2, **NO**, and H_2O are formed. The nitric acid should be concentrated. Test for the CO_2 by passing the gases into a solution of $BaCl_2$ containing **KOH**.

3.—H_3PO_2, H_3PO_3, and H_3PO_4 do not act upon oxalic acid.

4.—**Concentrated sulphuric acid,** with a gentle heat, decomposes *oxalic acid,* by removing the elements of water from it, with effervescence of *carbon dioxide and carbon monoxide:* $H_2C_2O_4 + H_2SO_4 = H_2SO_4.H_2O + CO_2 + CO$. With *oxalates,* the decomposition generates the same gases. Other strong dehydrating agents produce the same result.

The *effervescing gases,* CO_2 and **CO**, give the reactions for carbonic anhydride; also, if in a sufficient quantity, the **CO** will *burn with a blue flame,* when ignited.

5.—With **chlorine,** hydrochloric acid is formed and the oxalic acid becomes CO_2 (*Gmelin's Hand-book*, **9**, 116). This reaction takes place more readily in the presence of **KOH**, forming **KCl** and K_2CO_3. **HClO** forms CO_2 and **Cl**. If the oxalic be in excess **HCl** is formed. The action is more rapid in the presence of a fixed alkali, an alkali chloride and carbonate being formed. $HClO_3$ forms CO_2 and varying proportions of **Cl** and **HCl**, a high degree of heat and excess of oxalic acid favoring the production of **HCl** (Calvert and Davies, *J. C.*, 1850, **2**, 193).

6.—Bromine decomposes oxalic acid in alkaline mixture, forming a

bromide and a carbonate. In acid mixture a similar reaction takes place if a hot saturated solution of oxalic acid be used in excess. With $HBrO_3$, bromine and CO_2 are formed; with excess of oxalic acid and heat hydrobromic acid is formed.

7.—HIO_3 forms CO_2 and I. With mixtures of chlorates, bromates, and iodates, the chlorate is first decomposed, then the bromate, and finally the iodate (Guyard, *J. C.*, 1879, **36**, 593).

7. **Ignition.**—The oxalates are all dissociated on ignition. Those of the metals of the alkalis and alkaline earths are resolved at an incipient red heat, into carbonates and carbon monoxide (*a*)—a higher temperature decomposing the alkaline earth carbonates. The oxalates of metals, whose carbonates are easily decomposed, but whose oxides are stable, are resolved into oxides, carbonic anhydride, and carbon monoxide (*b*). The oxalates of metals, whose oxides are decomposed by heat, leave the metal, and give off carbonic anhydride (*c*). As an example of the latter class, *silver oxalate*, when heated before the blow-pipe, decomposes explosively, with a sudden puffing sound—a test for oxalates:

(*a*) $CaC_2O_4 = CaCO_3 + CO$
(*b*) $ZnC_2O_4 = ZnO + CO_2 + CO$
(*c*) $Ag_2C_2O_4 = 2Ag + 2CO_2$

8. **Detection.**—(*a*) By warming with concentrated sulphuric acid after decomposition of carbonates with dilute sulphuric acid: showing the presence of CO_2 by absorption in $Ca(OH)_2$ or in a solution of $BaCl_2$ alkaline with KOH; and showing the presence of CO by its combustibility. (*b*) In solution by precipitation in neutral, alkaline, or acetic acid solution by calcium chloride, and solubility of the precipitate in dilute hydrochloric acid. Frey (*Z.*, 1894, **33**, 533), recommends the formation of a zone of precipitation. To the HCl solution containing $BaCl_2$ and $CaCl_2$ he adds carefully a solution of $NaC_2H_3O_2$ and watches the zone of contact. (*c*) Warm the solution with dilute H_2SO_4 and $KMnO_4$. If the permanganate is not decolorized, $H_2C_2O_4$ is absent; if decolorized test for CO_2 with $Ca(OH)_2$.

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2.$$

9. **Estimation.**—(*a*) It is precipitated as CaC_2O_4; after washing, the Ca is determined by §188, 9, from which the oxalic acid is calculated. (*b*) By the amount of $KMnO_4$ which it will reduce. (*c*) By measuring the amount of CO_2 evolved when it is oxidized in any convenient manner, usually by MnO_2. (*d*) By the amount of gold it reduces from $AuCl_3$.

§228. Carbon dioxide. $CO_2 = 44.0$.

(Carbonic anhydride.)

Carbonic acid (*hypothetical*). $H_2CO_3 = 62.016$.

$C^{IV}O^{-''}_2$ and $H'_2C^{IV}O^{-''}_3$, $O=C=O$ and $H-O-\overset{\overset{O}{\|}}{C}-O-H$.

1. **Properties.**—The *specific gravity* of the gas CO_2 is 1.52897 (Crafts, *C. r.*, 1888, **106**, 162); of the liquid at —34°, 1.057 (Cailletet and Mathias, *C. r.*, 1886, **102**, 1202); of the solid (hammered), slightly under 1.2 (Landolt, *B.*, 1884, **17**, 309). *Critical temperature*, 30.92° (Andrews, *Trans. Roy. Soc.*, 1869, **159**, 583; 1876, **166**, 21). It is a heavy colorless gas; which at low temperatures, +3°, and high pressure, 79 atmospheres, may be condensed to a clear mobile liquid; and upon further cooling this becomes a snow-like mass. Liquid CO_2 is more compressible than other liquids (Natterer, *J.*, 1851, 59). It diffuses through porous plates more rapidly than oxygen (Graham, *C. N.*, 1863, **8**, 79). Non-combustible and a non-supporter of combustion, except that **K**, **Na** and **Mg** burn in the gas forming an oxide of the metal and free carbon. It is used in chemical fire engines. Non-poisonous but causes suffocation (drowning) by exclusion of air. It is taken internally without injury in soda water, etc.

Liquid CO_2 is insoluble in water which swims on the surface. It mixes with alcohol and ether. It dissolves iodine but does not dissolve phosphorus or sulphur; it is without action upon **K** or **Na**. A spirit thermometer immersed in the liquid registers —75° (Thilorier, *J. pr.*, 1834, **3**, 109). Solid CO_2 at 767.3 mm. barometric pressure *melts* at —77.94° (Regnault, *A. Ch.*, 1849, (3), **26**, 257). When the solid is mixed with ether it gives a temperature of —98.3°.

2. **Occurrence.**—In a free state in the air, about 0.04 per cent. Found in great abundance in the form of carbonates in the earth's crust; *e. g.*, limestone, marble, magnesite, dolomite, etc.

3. **Formation.**—(*a*) By burning wood, coal, etc., in the air. (*b*) By burning **CO**. (*c*) By the reduction of many metallic oxides upon ignition with charcoal. (*d*) During fermentation or decay of organic material. (*e*) By the reaction between acids and carbonates.

Liquid CO_2 is made by compressing the gas with pumps at a reduced temperature.

Solid CO_2 is made by allowing the liquid to escape freely into woolen bags and then compressing in wooden moulds (Landolt, *l. c.*).

4. **Preparation.**—$CaCO_3$ (chalk or marble) in small lumps is treated with hydrochloric acid in a Kipp's gas generating apparatus. The gas is passed through a solution of $NaHCO_3$ to remove any **HCl** that may be carried over, and then dried by passing through a tube filled with fused $CaCl_2$. It is also prepared on a large scale for making the liquid CO_2, and for use in sugar factories by the ignition of limestone: $CaCO_3 = CaO + CO_2$.

Preparation of Carbonates.—Na_2CO_3 is made by converting **NaCl** into Na_2SO_4, by treating it with H_2SO_4; then by long ignition with coal and calcium carbonate, impure sodium carbonate is formed (Leblanc's process).

$$Na_2SO_4 + 4C + CaCO_3 = CaS + 4CO + Na_2CO_3$$

It is separated by lixiviation with water, and farther purified. The other method, known as the ammonia, or Solvay's process, consists in passing NH_3 and CO_2 into a concentrated solution of NaCl (*a*). The $NaHCO_3$ is converted into Na_2CO_3 by heat, and the evolved CO_2 used over again (*b*). The NH_4Cl is warmed with MgO (*c*), and the NH_3 which is given off is used over again. The $MgCl_2$ is strongly heated (*d*) and the MgO is used over again, and the evolved gas sold as hydrochloric acid. This **continuous** process has nearly superseded the Leblanc process.

(*a*) $NaCl + NH_3 + H_2O + CO_2 = NaHCO_3 + NH_4Cl$

(*b*) $2NaHCO_3 + \text{heat} = Na_2CO_3 + CO_2 + H_2O$

(*c*) $2NH_4Cl + MgO = MgCl_2 + 2NH_3 + H_2O$

(*d*) $MgCl_2 + H_2O + \text{heat} = MgO + 2HCl$

The other carbonates are mostly made from the sodium salt (6).

5. **Solubilities.**—CO_2 is soluble in water, forming the hypothetical H_2CO_3, which reacts acid towards litmus. At 15° one volume of water absorbs 1.002 volumes of the gas (Bunsen, *A.*, 1855, **93**, 1). It is rapidly absorbed by hydroxides of the alkalis and of the alkaline earths, forming normal or acid carbonates: $KOH + CO_2 = KHCO_3$ or $2KOH + CO_2 = K_2CO_3 + H_2O$. The carbonates of the alkalis are soluble in water (acid alkali carbonates are less soluble than the normal carbonates), other carbonates are insoluble in water or only sparingly soluble. The presence of some other salts, especially ammonium salts, increases the solubility of carbonates, notably magnesium carbonate (§189, 5c). Many of the carbonates are soluble in water saturated with CO_2; forming acid carbonates of variable composition. Boiling removes the excess of CO_2, causing precipitation of the carbonate.

6. **Reactions.**—Dry carbon dioxide does not unite with dry calcium oxide at ordinary temperature (Birnbaum and Maher, *B.*, 1879, **12**, 1547; Scheibler, *B.*, 1886, **19**, 1973). Also at 0° no reaction takes place between dry CO_2 and dry Na_2O, but at 400° combination takes place with incandescence (Beketoff, *Bl.*, 1880, (2), **34**, 327).

Carbonates of the fixed alkalis precipitate solutions of all other metallic salts: with antimony the precipitate is an oxide; with tin, aluminum, chromium, and ferricum it is an hydroxide; with silver, mercurosum, cadmium, ferrosum, manganese, barium, strontium, and calcium it is a normal carbonate; with other metals a basic carbonate, except that mercuric chloride forms an oxychloride. Carbonic acid is completely displaced by strong acids, for example, from all carbonates, by HCl, $HClO_3$, HBr, $HBrO_3$, HI, HIO_3, $H_2C_2O_4$, HNO_3, H_3PO_4, H_2SO_4, and even by H_2S, completely from carbonates of the first four groups, incompletely from those of the fifth and sixth groups (Nandin and Montholon, *C. r.*, 1876, **33**, 58).

Ammonium carbonate precipitates solutions of all the non-alkali metals,

chiefly as carbonates; except magnesium salts which are not at all precipitated, a soluble double salt being at once formed (separation of barium, strontium, and calcium from magnesium). With salts of silver, copper, cadmium, cobalt, nickel, and zinc the precipitate is redissolved by an excess of the ammonium carbonate.

The decomposition of carbonates by acids is usually attended by marked effervescence of gaseous CO_2 which reddens moist litmus paper: $Na_2CO_3 + H_2SO_4 = Na_2SO_4 + H_2O + CO_2$.

With normal carbonates in cold solution, slight additions of acid (short of a saturation of half the base) do not cause effervescence, because acid carbonate is formed: $2Na_2CO_3 + H_2SO_4 = Na_2SO_4 + 2NaHCO_3$; and when there is much free alkali present (as in testing caustic alkalis for slight admixtures of carbonate), perhaps no effervescence is obtained. By the time all the alkali is saturated with acid, there is enough water present to dissolve the little quantity of gas set free. But if the carbonate *solution is added drop by drop to the acid*, so that the latter is constantly in excess, even slight traces of carbonate give notable effervescence.

The effervescence of carbonic acid gas, CO_2, is distinguished from that of H_2S or SO_2 by the gas being *odorless*, from that of N_2O_3 by its being *colorless* and odorless; from all others by the effervescence being proportionally more *forcible*. It should be remembered, however, that CO_2 is evolved (with CO) on adding strong sulphuric acid to *oxalates* or to cyanates.

On passing the gas, CO_2, into **solution of calcium hydroxide** (*a*); or of **barium hydroxide** (*b*); or into solutions of calcium or barium chloride, containing much ammonium hydroxide (*c*), or into **ammoniacal solution of lead acetate** (*d*), a white precipitate or turbidity of *insoluble carbonate* is obtained. The precipitate may be obtained by *decanting* the gas (one-half heavier than air) from the test-tube in which it is liberated into a (wide) test-tube, containing the solution to be precipitated; but the operation requires a little perseverance, with repeated generation of the gas, owing to the difficulty of displacing the air by pouring into so narrow a vessel. The result is controlled better by generating the gas in a large test-tube, having a stopper bearing a narrow delivery-tube, so bent as to be turned down into the solution to be precipitated.

(*a*) $CO_2 + Ca(OH)_2 = CaCO_3 + H_2O$

(*b*) $CO_2 + Ba(OH)_2 = BaCO_3 + H_2O$

(*c*) $CO_2 + CaCl_2 + 2NH_4OH = CaCO_3 + 2NH_4Cl + H_2O$

(*d*) $CO_2 + Pb_2O(C_2H_3O_2)_2 = PbCO_3 + Pb(C_2H_3O_2)_2$

The solutions of calcium and barium hydroxides furnish more *delicate tests for carbonic anhydride* than the ammoniacal solutions of calcium and barium chlorides, but less delicate than lead basic acetate solution. The latter is so rapidly precipitated by atmospheric carbonic anhydride, that

it cannot be preserved in bottles partly full and frequently opened, and cannot be diluted clear, unless with recently boiled water.

Solutions of the acid carbonates effervesce, with escape of CO_2, on **boiling or heating,** thus:

$2KHCO_3 = K_2CO_3 + H_2O + CO_2$. (Gradually, at 100°.)

$2NaHCO_3 = Na_2CO_3 + H_2O + CO_2$. (Gradually, at 70°; rapidly at 90° to 100°.)

$2NH_4HCO_3 = (NH_4)_2CO_3 + H_2O + CO_2$. (Begins to evolve CO_2 at 36°.)

$(NH_4)_4H_2(CO_3)_3 = 2(NH_4)_2CO_3 + H_2O + CO_2$. (Begins at 49°.)

7. **Ignition.**—On **ignition,** the normal carbonates of the metals of the fixed alkalis are not decomposed; the carbonates of barium and strontium are dissociated slowly, at white heat,* calcium carbonate at a full red heat, forming the oxide and CO_2. At a lower temperature, ignition changes all other carbonates to the oxide and CO_2, except that the carbonates of silver at 250°, mercury, and some of the rarer metals are reduced to the metallic state, CO_2 and oxygen being evolved. Stannous and ferrous oxides ignited in an atmosphere of CO_2 are changed to SnO_2 and Fe_2O_3, respectively, with evolution of **CO** (Wagner, *Z.*, 1879, **18,** 559).

8. **Detection.**—Carbonates are detected: (*a*) By the sudden effervescence when treated with dilute acids. (*b*) By the precipitate which this gas forms with solutions of $Ca(OH)_2$, $Ba(OH)_2$, or $Pb_2O(C_2H_3O_2)_2$. If but a small amount of carbonate be present, the mixture must be warmed to drive the CO_2 over into the reagent (6). A non-volatile acid as H_2SO_4 or H_3PO_4 should be used, as a volatile acid might pass over with the CO_2 and prevent the formation of a precipitate. (*c*) Phenolphthalein detects the normal carbonate in solution of the bicarbonate (very delicate). Sodium bicarbonate fails to give a precipitate with magnesium sulphate (distinction from Na_2CO_3) (Patein, *J. Pharm.*, 1892, (5), **25,** 448).

To detect free carbonic acid in presence of bicarbonates, a solution of 1 part of rosolic acid in 500 parts of 80 per cent alcohol may be employed, to which barium hydroxide has been added until it begins to acquire a red tinge. If 0.5 cc. of this rosolic acid solution be added to about 50 cc. of the water to be tested—spring water, for instance—the liquid will be colorless, or at most faintly yellowish if it contains free carbonic acid, whereas, if there be no free carbonic acid, but only double salts, it will be red (Pettenkofer, *Dingl.*, 1875, **217,** 158).

Salzer (*Z.*, 1881, **20,** 227) gives a test for free carbonic acid or bicarbonates in presence of carbonates, founded on the fact that the Nessler ammonia reaction (§**207,** 6*k*) does not take place in presence of free carbonic acid or bicarbonates. This reaction is also used to detect the presence of fixed alkali hydroxides in the fixed alkali carbonates. In presence of a

* Barium carbonate decomposes at 1450°; strontium carbonate at 1155°, and calcium carbonate at 825°.

fixed alkali hydroxide a brown precipitate is obtained (Dobbin, *J. Soc. Ind.*, 1888, **7**, 829).

9. **Estimation.**—(*a*) By decomposition of a weighed sample with a known weight of anhydrous borax or fused microcosmic salt ($NaPO_2$) and determining the CO_2 by loss of weight. (*b*) By decomposition of the weighed sample and collection of the CO_2 in a weighed **KOH** solution. (*c*) By decomposition with an excess of a standard acid, boiling to expel the CO_2 and titrating the excess of acid. (*d*) Sodium bicarbonate may be estimated by titration with sodium hydroxide: $NaHCO_3 + NaOH = Na_2CO_3 + H_2O$. The first excess of sodium hydroxide beyond the reaction gives a brown precipitate with silver nitrate (Lunge, *Z. angew.*, 1897, 169; Bohlig, *Arch. Pharm.*, 1888, **226**, 541).

§229. Cyanogen. $CN = 26.01$.

$$N \equiv C - C \equiv N.$$

A colorless, intensely poisonous gas; *specific gravity*, 1.8064 (Gay-Lussac, *Gilb.*, 1816, **53**, 145). The molecular weight shows the molecule to be C_2N_2. At ordinary atmospheric pressure it liquifies at —22° (Drion, *J.*, 1860, 41); at 20° under four atmospheres pressure (Hofmann, *B.*, 1870, **3**, 658). The gas has an odor of bitter almonds and burns with a red color to the flame forming CO_2 and **N**. When cooled to about the freezing point of mercury it solidifies to a crystalline ice-like mass (Hofmann, *l. c.*). *Critical temperature*, 124° (Dewar, *C. N.*, 1885, **51**, 27). The liquid is colorless, mobile and a non-conductor of electricity. It occurs in the gas from the coke ovens (Bunsen and Playfair, *J. pr.*, 1847, **42**, 145). It is prepared: (*a*) By heating the cyanides of mercury, silver or gold: $Hg(CN)_2 = Hg + C_2N_2$. (*b*) By the dry distillation of ammonium oxalate: $(NH_4)_2C_2O_4 = 4H_2O + C_2N_2$. (*c*) By fusing **KCN** with $HgCl_2$: $2KCN + HgCl_2 = Hg + 2KCl + C_2N_2$. (*d*) By heating a solution of $CuSO_4$ with **KCN**. Half of the **CN** is evolved and **CuCN** is formed. If the **CuCN** be heated with $FeCl_3$ or MnO_2 and $HC_2H_3O_2$, the remainder of the **CN** is obtained. The gas is purified by absorption with aniline; oxygen, nitrogen and carbon dioxide are not absorbed (Jacquemin, *A. Ch.*, 1886, (6), **6**, 140). It combines with **Cl**, **Br**, **I**, **S**, **P**, and with many of the metals, reacting very much like the halogens. It dissolves in water, alcohol and ether; but gradually decomposes with formation of ammonium oxalate and carbonate (Vauquelin, *A. Ch.*, 1823, **22**, 132; Buff and Hofmann, *A.*, 1860, **113**, 129). At 500° it combines with hydrogen to form **HCN** (Berthelot, *Bl.*, 1880, (2), **33**, 2). With **Zn** it forms $Zn(CN)_2$, rapidly at 100°. With **HCl** and absolute alcohol it forms oxalic ether, which shows cyanogen to be the nitrile of oxalic acid (Pinner and Klein, *B.*, 1878, **11**, 1481). With solution of **KOH**, **KCN** and **KCNO** are formed: $C_2N_2 + 2KOH = KCN + KCNO + H_2O$. Compare the reaction with chlorine and **KOH** (§270).

§230. Hydrocyanic acid. $HCN = 27.018$.

$$H - C \equiv N.$$

1. **Properties.**—Hydrocyanic acid is a clear, mobile liquid, boiling at 26°. At —15° it freezes to a fibrous crystalline mass. *Specific gravity* at 19°, 0.697 (Bleekrode, *Proc. Roy. Soc.*, 1884, **37**, 339). It burns with a bluish-red flame, forming H_2O, CO_2 and **N**. Its index of refraction is much less than that of water (Mascart, *C. r.*, 1878, **86**, 321). It is one of the most active poisons known; of a very characteristic odor, somewhat resembling that of bitter almonds. The antidote is chlorine or ammonia by inhalation. Its water solution decomposes slowly, forming ammonium formate; scarcely at all in the dark. It distils readily unchanged. The U. S. P. solution contains two per cent of **HCN**. It is a weak acid, scarcely reddening litmus; its salts are partially decomposed by CO_2. The free acid or soluble salts when warmed

with dilute alkalis or acids (with strong acids in the cold) becomes formic acid and ammonia: $HCN + 2H_2O = HCO_2H + NH_3$.

2. **Occurrence.**—The free acid does not occur in nature, but in combination in the kernels of bitter almonds, peaches, apricots, plums, cherries and quinces; the blossoms of the peach, sloe and mountain ash; the leaves of the peach, cherry laurel and Portugal laurel; the young branches of the peach; the stem-bark of the Portugal laurel and mountain ash; and the roots of the last-named tree, when soaked in water for a time and then distilled, yield hydrocyanic acid, together with bitter-almond oil. Potassium cyanide appears in the deposits of blast furnaces for the smelting of iron ores.

3. **Formation.**—(*a*) Decomposition of amygdaline by emulsine and distillation. (*b*) By the action of the electric spark on a mixture of acetylene and nitrogen (Berthelot, *J.*, 1874, 113). (*c*) By heating a mixture of cyanogen and hydrogen (§229). (*d*) By the dry distillation of ammonium formate: $NH_4CHO_2 = HCN + 2H_2O$. (*e*) By boiling or fusing many organic compounds containing nitrogen with KOH, forming KCN (Post and Huebner, *B.*, 1872, **5**, 408). (*f*) By decomposition of metallic cyanides with mineral acids. (*g*) By heating chloroform with a mixture of ammonium and potassium hydroxides (Hofmann, *A.*, 1867, **144**, 116).

4. **Preparation.**—(*a*) By the action of dilute sulphuric acid on potassium ferrocyanide: $2K_4Fe(CN)_6 + 3H_2SO_4 = 6HCN + K_2Fe_2(CN)_6 + 3K_2SO_4$. (*b*) By action of acids upon metallic cyanides. (*c*) By the action of sulphuric acid upon mercuric cyanide in the presence of metallic iron: $Hg(CN)_2 + Fe + H_2SO_4 = 2HCN + FeSO_4 + Hg$.

Metallic cyanides are prepared: (*a*) By the action of HCN on metallic hydroxides. (*b*) By the action of soluble cyanides on metallic salts. (*c*) By igniting potassium ferrocyanide: $K_4Fe(CN)_6 = 4KCN + FeC_2 + N_2$. (*d*) By heating potassium ferrocyanide with potassium carbonate. If prepared in this manner it contains some cyanate: $K_4Fe(CN)_6 + K_2CO_3 = 5KCN + KCNO + Fe + CO_2$.

5. **Solubilities.**—Hydrocyanic acid is soluble in water, alcohol and ether in all proportions. A mixture of equal parts acid and water increases in temperature from 14° to 22.5°; it also increases slightly in volume (Bussy and Buignet, *A. Ch.*, 1865, (4), **4**, 4).

The **cyanides** of the alkali metals, alkaline earth metals, and mercuric cyanide, are **soluble in water**, barium cyanide being but sparingly soluble. The solutions are alkaline to test-paper. The other metallic cyanides are insoluble in water. Many of these dissolve in solutions of alkali cyanides, by combination, as *double metallic cyanides.*

Pb, **Hg**, **As**, **Sb**, **Sn**, **Bi** and **Cd** are dissolved by **KCN** with absorption of oxygen. **Cu**, **Al**, **Fe** (by **H** or **CO**), **Co**, **Ni**, **Zn** and **Mg** with evolution of hydrogen: $2Cu + 2KCN + 2H_2O = 2CuCN + 2KOH + H_2$. Iron or steel wire are not attacked (Goyder, *C. N.*, 1894, **69**, 262, 268 and 280).

6. **Reactions.**—There are two classes of **double cyanides**, both of which are formed when a cyanide is precipitated by an alkali cyanide, and redissolved by excess of the precipitant: $HgCl_2 + 2KCN = Hg(CN)_2 + 2KCl$; and with excess of KCN: $Hg(CN)_2 + 2KCN = (KCN)_2Hg(CN)_2$.

Class I. Double cyanides *which are not affected by alkali hydroxides, but are decomposed when treated with dilute acids:* $(KCN)_2Hg(CN)_2 + 2HCl = Hg(CN)_2 + 2KCl + 2HCN$. These closely resemble the double iodides (potassium mercuric), and the double sulphides or thiosalts (§69, 5*c* and 6*e*). The most frequently occurring of the double cyanides of this class, which dissolve in water, are given below:

Potassium (or sodium) zinc cyanide, $K_2Zn(CN)_4$ or $(KCN)_2Zn(CN)_2$.
Potassium (or sodium) nickel cyanide, $K_2Ni(CN)_4$ or $(KCN)_2Ni(CN)_2$.
Potassium (or sodium) copper cyanide, $K_2Cu(CN)_3$ or $(KCN)_2CuCN$.
Potassium cadmium cyanide, $K_2Cd(CN)_4$ or $(KCN)_2Cd(CN)_2$.
Potassium (sodium or ammonium) silver cyanide, $KAg(CN)_2$ or KCNAgCN.
Potassium (or sodium) mercuric cyanide, $K_2Hg(CN)_4$ or $(KCN)_2Hg(CN)_2$.
Potassium (or sodium) auric cyanide, $KAu(CN)_4$ or $KCNAu(CN)_3$.

Class II. Double cyanides *which, as precipitates, are transposed by alkali hydroxides, in dilute solution* (*a*), *and are transposed, without decomposition, by dilute acids* (*b*). In these double cyanides, as potassium ferrous cyanide, $K_4Fe(CN)_6$, the whole of

the cyanogen appears to form *a new compound radical* with that metal whose single cyanide is insoluble in water; thus, $Fe(CN)_6$ as "ferrocyanogen," giving $K_4Fe(CN)_6$ as "potassium ferrocyanide" (for the potassium ferrous cyanide). These more stable double cyanides or "ferrocyanides," etc., correspond to the platinic double chlorides or "chloroplatinates" (§74, 5*c*), and the palladium double chlorides, or chloropalladiates (§106, 5*c*). The most frequently occurring of the double cyanides of this class, which are soluble in water, are given below.

(*a*) $Cu_2Fe(CN)_6 + 4KOH = 2Cu(OH)_2 + K_4Fe(CN)_6$

(*b*) $K_4Fe(CN)_6 + 2H_2SO_4 = 2K_2SO_4 + H_4Fe(CN)_6$

$2K_3Fe(CN)_6 + 3H_2SO_4 = 3K_2SO_4 + 2H_3Fe(CN)_6$

Alkali ferrocyanides, as $K_4Fe''(CN)_6$, potassium ferrocyanide.
Ferricyanides, as $K_3Fe'''(CN)_6$, potassium ferricyanide.
Cobalticyanides, as $K_3Co'''(CN)_6$, potassium cobalticyanide.
Manganicyanides, as $K_3Mn'''(CN)_6$, potassium manganicyanide.
Chromicyanides, as $K_3(Cr''')(CN)_6$, potassium chromicyanide.

The easily decomposed double cyanides of Class I are, like the single cyanides, intensely poisonous. The difficultly decomposed double cyanides of Class II. are not poisonous.

The **Single Cyanides** are transposed by the **stronger mineral acids,** more or less readily, with liberation of *hydrocyanic acid,* **HCN,** effervescing from concentrated or hot solutions, remaining dissolved in cold and dilute solutions. Mercuric cyanide furnishes **HCN** by action of H_2S, not by other acids. The cyanides of the alkali and alkaline earth metals are decomposed by all acids—even the carbonic acid of the air—and exhale the odor of hydrocyanic acid. Solution of silver nitrate precipitates, from solutions of cyanides or of hydrocyanic acid (not from mercuric cyanide) *silver cyanide,* **AgCN**, white, insoluble in dilute nitric acid, soluble in ammonium hydroxide, in hot ammonium carbonate, in potassium cyanide, and in thiosulphates—uniform with silver chloride. Cold strong hydrochloric acid decomposes it with evolution and odor of hydrocyanic acid (recognition *from chloride*); and when well washed, and then gently ignited, it does not melt, but leaves metallic silver, soluble in dilute nitric acid, and precipitable as chloride (distinction and means of separation from chloride).

Solution of **mercurous nitrate,** with cyanides or hydrocyanic acid, is resolved into *metallic mercury,* as a gray precipitate, and mercuric cyanide and nitrate, in solution. Salts of **copper** react, as stated in §77, 6*b;* **salts of lead,** as stated in §57, 6*b.*

Ferrous salts, added to saturation, precipitate from solutions of cyanides, not from hydrocyanic acid, *ferrous cyanide,* $Fe(CN)_2$, white, if free from the ferric hydroxide formed by admixture of ferric salt, and, with the same condition, soluble in excess of the cyanide, as (with potassium cyanide), $(KCN)_4Fe(CN)_2 = K_4Fe(CN)_6$, potassium *ferrocyanide* (*a*). On acidulating this solution, it gives the blue precipitates with ferric salts (*b*):

(*a*) $2KCN + FeSO_4 = Fe(CN)_2 + K_2SO_4$

$Fe(CN)_2 + 4KCN = K_4Fe(CN)_6$

(*b*) $3K_4Fe(CN)_6 + 4FeCl_3 = Fe_4(Fe(CN)_6)_3 + 12KCl$

This *production of the blue ferric ferrocyanide is made a delicate test for*

hydrocyanic acid, as follows: A little potassium hydroxide and ferrous sulphate are added, the mixture digested warm for a short time; then a very little ferric chloride is added, and the whole slightly acidulated (so as to dissolve all the ferrous and ferric hydroxides), when Prussian blue will appear, if hydrocyanic acid was present (Link and Moeckel, *Z.*, 1878, **17,** 456. For identification of traces of hydrocyanic acid (less than 0.00002 g. in 1 c.c.) add two drops of 10% solution of sodium hydroxide, evaporate almost to dryness, cool, add one drop of a 2% solution of ferric sulphate and allow to stand in the cold for 10-15 minutes. Heat gently with two or three drops of strong hydrochloric acid and cool. The undiluted blue-green solution shows, when carefully diluted, a blue color. (G. Druce Lander und Walden, nach *Leitschr. J. Unters. d. Nahrungs u. Genussm.* **23** [1912] 399.)

Solution of **nitrophenic acid,** *picric acid,* $C_6H_2(NO_2)_3OH$, added, in a small quantity, to a neutralized solution of cyanides of alkali metals, on boiling(and standing), gives a blood-red color, due to picrocyanate (as $KC_8H_4N_5O_6$). This test is very delicate, but not very distinctive, as various reducing agents give red products with nitrophenic acid (Vogel, *C. N.,* 1884, **50,** 270).

The **fixed alkali hydroxides,** in boiling solution, strongly alkaline, gradually decompose the cyanides with production of *ammonia* and formate: $HCN + KOH + H_2O = KCHO_2 + NH_3$. Ferrocyanides and ferricyanides finally yield the same products. Dilute alkalis, not heated, transpose, as by equation *a*, class II above.

Cyanides are strong reducing agents. The action is not so marked in solution as in state of fusion (7). Permanganates are reduced by cyanides, and cupric hydroxide in alkaline solution forms Cu′. Solutions of cyanides on exposure to the air take up some oxygen with formation of a cyanate: $2KCN + O_2 = 2KCNO$. Commercial potassium cyanide always contains some potassium cyanate. By warm digestion of a **cyanide** with **sulphur** or with yellow ammonium sulphide a thiocyanate is formed (8). Hydrocyanic acid reduces PbO_2, forming $Pb(CN)_2$ and CN : $PbO_2 + 4HCN = Pb(CN)_2 + C_2N_2 + 2H_2O$ (Liebig, *A.*, 1838, **25,** 3). With **HCN** and H_2O_2 oxamide is formed (Altfield, *J. C.*, 1863, **16,** 94). Chlorine forms with hydrocyanic acid a cyanogen chloride (Serullas, *A. Ch.*, 1828, **38,** 370); with iodine the reaction is not so marked, but a similar product is formed (Meyer, *B.*, 1887, **20,** III, 704). Concentrated sulphuric acid decomposes all cyanides.

7. **Ignition.**—By fusion with fixed alkalis, cyanides and all compounds containing cyanogen yield ammonia. In state of fusion cyanides are very efficient reagents for reduction of metals from their oxides or sulphides

to the metallic state (§69, 7). The cyanates or thiocyanates formed in the reaction are not readily decomposed by heat alone.

8. **Detection.**—Cyanides may be detected: (*a*) By the odor of the free acid upon decomposition of the cyanide with acids. This test must be applied with extreme caution as the evolved **HCN** or **CN** is very poisonous. (*b*) By formation of a ferrocyanide and its reaction with ferric salts, as described in 6. (*c*) *The production of the red ferric thiocyanate is a test for hydrocyanic acid, more delicate* than formation of ferrocyanide. By warm digestion this reaction occurs: $2KCN + S_2 = 2KCNS$; or:

$$2(NH_4)_2S_4 + 4HCN = 4NH_4CNS + 2H_2S + S_2$$

To the material in an evaporating-dish, add one or two drops of **yellow ammonium sulphide**, and digest on the water-bath until the mixture is colorless, and free from sulphide. Slightly acidulate with hydrochloric acid (which should not liberate H_2S), and add a drop of solution of ferric chloride; the blood-red solution of ferric thiocyanate will appear, if hydrocyanic acid was present (Link and Moeckel, *l. c.*).

(*d*) Link and Moeckel also recommend the following test for cyanides, delicate to 1-3,000,000. Saturate a filter paper with a four per cent alcoholic solution of guaiac; allow the alcohol to evaporate; then moisten the paper with a one-fourth per cent solution of copper sulphate, and allow the unknown solution to trickle over this test paper. A deep blue color indicates the presence of a cyanide.

To detect cyanides in presence of ferri- and ferrocyanides it is directed to add tartaric acid and, in a distilling flask, pass a current of carbon dioxide, warming not above 60°. Test the distillate by the methods given above. Ferro- and ferricyanides do not yield **HCN** under 80° (Hilger and Tamba, *Z.*, 1891, **30**, 529; also Taylor, *C. N.*, 1884, **50**, 227).

9. **Estimation.**—(*a*) The nearly neutral solution of cyanide is titrated with standard silver nitrate. No precipitate occurs as long as two molecules of alkali cyanide are present to one of silver nitrate. Soluble **AgCN.KCN** is formed. As soon as the alkali cyanide is all used in the formation of the double cyanide, the next molecule of silver nitrate decomposes a molecule of the double salt, forming two molecules of insoluble silver cyanide; giving a white precipitate for the end reaction. Chlorides do not interfere (Liebig, *A.*, 1851, **77**, 102). (*b*) By titration with a standard solution of $HgCl_2$, applicable in presence of cyanates and thiocyanates (Hannay, *J. C.*, 1878, **33**, 245).

§231. Hydroferrocyanic acid. $H_4Fe(CN)_6 = 215.932$.

$$H'_4Fe''(CN)^{-\prime}{}_6.$$

Absolute hydroferrocyanic acid (§230, 6, Class II.), is a white solid, freely soluble in water and in alcohol. The solution is strongly acid to test-paper, and decomposes carbonates, with effervescence, and acetates. It is non-volatile, but absorbs oxygen from the air, more rapidly when heated, evolving hydrocyanic acid and depositing Prussian blue: $7H_4Fe(CN)_6 + O_2 = Fe_4(Fe(CN)_6)_3 + 2H_2O + 24HCN$.

Potassium ferrocyanide is the usual starting point in the preparation of the

free acid or any of the salts. It is prepared by fusing together in an iron kettle nitrogenous animal matter (blood, hair, horn, hoof, etc.), commercial potash (KOH), and scrap iron. The ferrocyanide is formed when this mass is digested with water. The filtrate is evaporated to crystallization (lemon-yellow prism), soluble in four parts of water.

Hydroferrocyanic acid is formed by transposition of metallic ferrocyanides in solution, with strong acids (*a*). When the solution is heated, hydrocyanic acid is evolved; in the case of an alkali ferrocyanide, without absorption of oxygen (*b*). Potassium ferrocyanide and sulphuric acid are usually employed for preparation of hydrocyanic acid (*c*):

(*a*) $K_4Fe(CN)_6 + 2H_2SO_4 = 2K_2SO_4 + H_4Fe(CN)_6$

(*b*) $3H_4Fe(CN)_6 + K_4Fe(CN)_6 = 2K_2FeFe(CN)_6 + 12HCN$

(*c*) $2K_4Fe(CN)_6 + 3H_2SO_4 = 3K_2SO_4 + K_2FeFe(CN)_6 + 6HCN$

The ferrocyanides of the alkali metals, strontium, calcium and magnesium, are freely soluble in water; of barium, sparingly soluble; of the other metals, insoluble in water. There are *double ferrocyanides*; soluble and insoluble; that of barium and potassium is soluble, but *potassium calcium ferrocyanide* is insoluble. The most of the ferrocyanides of a heavy metal and an alkali metal are insoluble. Potassium and sodium ferrocyanides are precipitated from their water solutions by alcohol (distinction from ferricyanides).

The soluble ferrocyanides are yellowish in solution and in crystals, white when anhydrous. The *insoluble ferrocyanides* have marked and very diverse colors, as seen below.

Solutions of alkali ferrocyanides, as $K_4Fe(CN)_6$, give, with soluble salts of:

Aluminum,	a white precipitate,	$Al(OH)_3$ and $Fe(CN)_2$ (formed slowly).
Antimony	a white "	$Sb_4[Fe(CN)_6]_3.25H_2O$.
Bismuth,	a white "	$Bi_4(Fe(CN)_6)_3$.
Cadmium,	a white "	$Cd_2Fe(CN)_6$ (soluble in HCl).
Calcium,	a white "	$K_2CaFe(CN)_6$.
Chromium,	no "	
Cobalt,	a green, then gray "	$Co_2Fe(CN)_6$.
Copper,	a red-brown "	$Cu_2Fe(CN)_6$.
Gold,	no "	
Iron (Fe″),	white, then blue "	$K_2FeFe(CN)_6$.
Iron (Fe‴),	a deep blue "	$Fe_4(Fe(CN)_6)_3$.
Lead,	a white "	$Pb_2Fe(CN)_6$.
Magnesium,	a white "	$(NH_4)_2MgFe(CN)_6$ (in presence of NH_4OH)
	a yellow-white "	$K_2MgFe(CN)_6$ (only in concentrated solution).
Manganese,	a white "	$Mn_2Fe(CN)_6$ (soluble in HCl).
Mercury (Hg′),	a white "	$Hg_4Fe(CN)_6$ (gelatinous).
Mercury (Hg″),	a white "	$Hg_2Fe(CN)_6$, turning to $Hg(CN)_2$ and $Fe_3(Fe(CN)_6)_2$, blue.
Molybdenum,	a brown "	
Nickel,	a greenish-white "	$Ni_2Fe(CN)_6$.
Silver,	a white "	$Ag_4Fe(CN)_6$, (slowly turning blue).
Tin (Sn″ and Sn^{IV}),	white "	(gelatinous).
Uranium (uranous),	brown "	$UFe(CN)_6$.
Uranium (uranyl),	red-brown "	$(UO_2)_2Fe(CN)_6$.
Zinc,	a white, gelatinous "	$Zn_2Fe(CN)_6$.

See Wyrouboff (*A. Ch.*, 1876 (5), **8**, 444; and 1877, (5), **10**, 409).

Insoluble ferrocyanides are transposed by alkalis (§230, 6, Class II.)

It will be observed (§230, 6) that *ferrocyanides are ferrous* combinations, while *ferricyanides are ferric* combinations. And, although ferrocyanides are far less easily oxidized than simple ferrous salts, being stable in the air, they are

nevertheless **reducing agents**, of moderate power: $2K_4Fe(CN)_6 + Cl_2 = 2K_3Fe(CN)_6 + 2KCl$.

PbO_2 with sulphuric acid forms Pb″ and $H_3Fe(CN)_6$.

Ag′ with fixed alkali forms an alkali ferricyanide and metallic silver.

Cr^{VI} with phosphoric acid, gives Cr‴ and $H_3Fe(CN)_6$ (Schönbein, *J. pr.*, 1840, **20**, 145).

Co‴ with phosphoric acid forms Co″ and $H_3Fe(CN)_6$.

Ni‴ with acetic acid gives Ni″ and $H_3Fe(CN)_6$.

MnO_2 with phosphoric acid gives Mn″ and $H_3Fe(CN)_6$.

Mn^{VII} forms with potassium hydroxide MnO_2 and potassium ferricyanide. With sulphuric acid, manganous sulphate and hydroferricyanic acid.

Ferricyanides when boiled with NH_4OH give ferrocyanides (Playfair, *J. C.*, 1857, **9**, 128).

HNO_2 forms first hydroferricyanic acid, then hydronitroferricyanic acid and NO.

HNO_3 forms hydroferricyanic acid, and then hydronitroferricyanic acid, NO being evolved.

Cl forms first hydroferricyanic and hydrochloric acids. Excess of chlorine to be avoided in preparation of ferricyanides.

$HClO_3$ forms hydroferricyanic and hydrochloric acids.

Br forms hydroferricyanic and hydrobromic acids.

$HBrO_3$ forms hydroferricyanic and hydrobromic acids.

I, iodine is decolored by potassium ferrocyanide, and some potassium ferricyanide and potassium iodide are formed. The action is slow and never complete (*Gmelin's Hand-book*, **7**, 459).

HIO_3 forms hydroferricyanic acid and free iodine.

In **analysis**, soluble ferrocyanides are recognized by their reactions with ferrous and ferric salts and copper salts (see 6*b*, §126 and §77). Separated from ferricyanide, by insolubility of alkali salt in alcohol. Separation of hydroferrocyanic acid from hydroferricyanic acid according to Ph. E. Browning and H. E. Palmer (*Zeitschr. f. anorg. chem.*, **54**, 315, *nach. Zeitschr. f. anal. chem.*, **50** (1911) 771). Acidify 5–10 c.c. of the solution which is to be tested with acetic or hydrochloric acid and add a solution of a thorium salt. Thorium ferrocyanide will be precipitated. Shake up with finely divided asbestos, filter, wash the precipitate, add sodium hydroxide to same and in this filtrate test for ferrocyanide.

To the filtrate from the thorium ferrocyanide add a solution of a cadmium salt. Cadmium ferricyanide will be precipitated and is treated like thethorium precipitate.

Ferrocyanides are estimated in solution with sulphuric acid by titrating with standard $KMnO_4$. Also by precipitation with $CuSO_4$ either for gravimetric determination or volumetrically, using a ferric salt as an external indicator.

§232. Hydroferricyanic acid. $H_3Fe(CN)_6 = 214.924$.

$$H'_3Fe'''(CN)^{---}_6.$$

Absolute hydroferricyanic acid, $H_3Fe(CN)_6$, is a non-volatile, crystallizable solid, readily soluble in water, with a brownish color, and an acid reaction to test-paper. It is decomposed by a slight elevation of temperature. In the transposition of most ferricyanides, by sulphuric or other acid, the hydroferricyanic acid radical is broken up.

Potassium ferricyanide is the usual starting point in the preparation of most ferricyanides. It is prepared by passing chlorine into a cold solution of $K_4Fe(CN)_6$ until a few drops of the liquid gives a brownish color, but no precipitate with a ferric salt. The solution is evaporated to crystallization and the salt repeatedly recrystallized from water as large red prismatic crystals, very soluble in water, freely soluble in alcohol (distinction from $K_4Fe(CN)_6$). The free acid is made by adding to a cold saturated solution of $K_3Fe(CN)_6$ three volumes of concentrated HCl and drying the precipitate which forms, in a vacuum (Joannis, *C. r.*, 1882, **94**, 449, 541 and 725) lustrous, brownish-green needles, very soluble in water and alcohol, insoluble in ether.

The **ferricyanides** of the metals of the alkalis and alkaline earths are **soluble in water**; those of most of the other metals are insoluble or sparingly soluble. The soluble ferricyanides have a red color, both in crystals and solution; those insoluble have different, strongly marked colors. Potassium and sodium ferri-

cyanides are but slightly, or not at all, precipitated from their water solutions by **alcohol** (separation from ferrocyanides).

Ferricyanides are not easily decomposed by dilute acids; but alkali hydroxides, either transpose them or decompose their radicals (§230, 6).

Solutions of metallic **ferricyanides** give, with soluble salts of:

Aluminum, no precipitate.

Antimony, no precipitate.

Bismuth, light-brown precipitate, $BiFe(CN)_6$, insoluble in **HCl**.

Cadmium, yellow precipitate, $Cd_3[Fe(CN)_6]_2$, soluble in acids and in ammonium hydroxide.

Chromium, no precipitate.

Cobalt, brown-red precipitate, $Co_3[Fe(CN)_6]_2$, insoluble in acids. With ammonium chloride and hydroxide, excess of ferricyanide gives a blood-red solution, a distinction of cobalt, from nickel, manganese and zinc.

Copper, a yellow-green precipitate, $Cu_3[Fe(CN)_6]_2$, insoluble in **HCl**.

Gold, no precipitate.

Iron (ferrous), *dark blue precipitate*, $Fe_3[Fe(CN)_6]_2$, insoluble in acids.

Iron (ferric), *no precipitate*, a darkening of the liquid.

Lead, no precipitate, except in concentrated solutions (dark brown).

Manganese, brown precipitate, $Mn_3[Fe(CN)_6]_2$, insoluble in acids.

Mercury (mercurous), red-brown precipitate, turning white on standing.

Mercury (mercuric), no precipitate.

Nickel, yellow-green precipitate, $Ni_3[Fe(CN)_6]_2$, insoluble in hydrochloric acid. With ammonium chloride and hydroxide, excess of ferricyanide gives a copper-red precipitate.

Silver, a red-brown precipitate, $Ag_3Fe(CN)_6$, soluble in NH_4OH.

Tin (stannous), white precipitate, $Sn_3[Fe(CN)_6]_2$, soluble in hydrochloric acid.

Tin (stannic), no precipitate.

Uranium (uranous), no precipitate.

Zinc, orange precipitate, $Zn_3[Fe(CN)_6]_2$, soluble in **HCl** and in NH_4OH.

Ferricyanides, ferric combinations, are capable of acting as oxidizing agents, becoming ferrocyanides, ferrous combinations.

$$4K_3Fe(CN)_6 + 2H_2S = 3K_4Fe(CN)_6 + H_4Fe(CN)_6 + S_2$$
$$2K_3Fe(CN)_6 + 2KI = 2K_4Fe(CN)_6 + I_2.$$

Nitric acid, or acidulated nitrite, by continued digestion in hot solution, effects a still higher **oxidation of ferricyanides**, with the production, among other products, of *nitroferricyanides* or *nitroprussides* (Playfair, *Phil. Mag.*, 1845, (3), **26**, 197, 271 and 348). These salts are generally held to have the composition represented by the acid $H_2Fe(NO)(CN)_5$. *Sodium nitroprusside* is used as a reagent for soluble sulphides that is, in presence of alkali hydroxides, a test for hydrosulphuric acid; in presence of hydrosulphuric acid, a test for alkali hydroxides (§207, 6*b*).

$K_3Fe(CN)_6$ is reduced to $K_4Fe(CN)_6$ by **Pd**, **Th**, **Mg** and **As**, but not by **Pb**, **Hg**, **Ag**, **Sb**, **Sn**, **Au**, **Pt**, **Bi**, **Cu**, **Cd**, **Te**, **Al**, **Fe**, **Co**, **Mn**, **Zn** and **In**. When a sheet of any metal except **Au** and **Pt** is placed in contact with a solution of $K_3Fe(CN)_6$ and $FeCl_3$, a coating of Prussian blue is soon formed (Boettger, *J. C.*, 1873, **26**, 473).

Pb″ with potassium hydroxide forms PbO_2 and potassium ferrocyanide (*Watts' Dictionary*, 1889, **2**, 340).

Sn″ with potassium hydroxide forms potassium stannate, K_2SnO_3 and potassium ferrocyanide (*Watts' Dictionary*, *l. c.*).

Cr‴ forms in alkaline mixture a chromate and a ferrocyanide (Bloxam, *C. N.*, 1885, **52**, 109).

Mn″ with potassium hydroxide forms MnO_2 and potassium ferrocyanide (Boudault, *J. pr.*, 1845, **36**, 23).

Co″ and **Ni″** are not oxidized.

In alkaline solutions $K_3Fe(CN)_6$ oxidizes sugar, starch, alcohol, oxalic acid and indigo (Wallace, *J. C.*, 1855, **7**, 77; Mercer, *Phil. Mag.*, 1847, (3), **31**, 126).

HNO_2 and HNO_3 both form hydronitroferricyanic acid, $H_2Fe(NO)(CN)_5$.

NO in alkaline solution becomes a nitrate (Wallace, *l. c.*).
P in alkaline solution becomes a phosphate (Wallace, *l. c.*).
HH_2PO_2 forms $H_4Fe(CN)_6$ and H_3PO_4.
H_2S forms **S**, then H_2SO_4 and $H_4Fe(CN)_6$ (Wallace, *l. c.*).
SO_2 forms H_2SO_4 and $H_4Fe(CN)_6$.
Cl decomposes ferricyanides.
$HClO_3$ acts upon $K_3Fe(CN)_6$, forming potassium superferricyanide, $K_2Fe(CN)_6$ (Skraup, *A.*, 1877, **189**, 368).
HI forms $H_4Fe(CN)_6$ and **I**.

Ferricyanides in solution are detected by the reactions with ferrous and ferric salts (§126, 6*b*). Insoluble compounds are ignited (under a hood) with a fixed alkali, giving an alkali cyanide, ferric oxide, and an oxide of the metal in combination. Detect the alkali cyanide as directed (§230, 8). A ferricyanide is estimated by reduction to ferrocyanide with **KI** in presence of concentrated **HCl**; the liberated iodine being titrated with standard $Na_2S_2O_3$. Or it is reduced to ferrocyanide by boiling with **KOH** and $FeSO_4$, filtering, acidulating with H_2SO_4 and titrating with $KMnO_4$.

§233. Cyanic acid. HCNO = 23.018.

$$H-O-C\equiv N.$$

The cyanates of the alkalis and of the fourth-group metals may be made by passing cyanogen gas into the hydroxides. The cyanates of the alkalis are easily prepared by fusion of the cyanide with some easily reducible oxide.

$$C_2N_2 + 2KOH = KCNO + KCN + H_2O$$
$$KCN + PbO = KCNO + Pb$$
$$4KCN + Pb_3O_4 = 4KCNO + 3Pb$$

The free acid may be obtained by heating cyanuric acid, $H_3C_3N_3O_3$, to redness, better in an atmosphere of CO_2. Cyanic acid is found in the distillate. $H_3C_3N_3O_3 = 3HCNO$.

Absolute cyanic acid, **HCNO**, is a colorless liquid, giving off pungent, irritating vapor, and only preserved at very low temperatures. It cannot be formed by transposing metallic cyanates with the stronger acids in the presence of water, by which it is changed into carbonic anhydride and ammonia: $HCNO + H_2O = NH_3 + CO_2$. The **cyanates**, therefore, when treated with hydrochloric or sulphuric acid, effervesce with the escape of *carbonic anhydride* (distinction from cyanides), the pungent *odor of cyanic acid* being perceptible: $2KCNO + 2H_2SO_4 + 2H_2O = K_2SO_4 + (NH_4)_2SO_4 + 2CO_2$. The *ammonia* remains in the liquid as ammonium salt, and may be detected by addition of potassium hydroxide, with heat.

The cyanates of the metals of the alkalis and of calcium are soluble in water; most of the others being insoluble or sparingly soluble. All the solutions gradually decompose, with evolution of ammonia. *Silver cyanate* is sparingly soluble in hot water, readily soluble in ammonia; soluble, with decomposition, in dilute nitric acid (distinction from cyanide). *Copper cyanate* is precipitated greenish-yellow.

Ammonium cyanate in solution changes gradually, or immediately when boiled, to *urea*, or carbamide, with which it is isomeric: $NH_4CNO = CO(NH_2)_2$. The latter is recognized by the characteristic crystalline laminæ of its nitrate, when a few drops of the solution, on glass, are treated with a drop of nitric acid. Also, solution of urea with solution of mercuric nitrate, forms a white precipitate, $CH_4N_2O(HgO)_2$, not turned yellow (decomposed) by solution of sodium carbonate (no excess of mercuric nitrate being taken). Solution of urea, on boiling, is resolved into ammonium carbonate, which slowly vaporizes: $CH_4N_2O + 2H_2O = (NH_4)_2CO_3$. Cyanates, in the dry way, are reduced by strong deoxidizing agents to cyanides.

For detection of a cyanate in presence of cyanides, see Schneider, *B.*, 1895, **28**, 1540.

§234. Thiocyanic acid. $HCNS = 59.088$.

$$H-S-C\equiv N.$$

An aqueous solution of **HCNS** may be obtained by treating lead thiocyanate suspended in water with H_2S, also by treating barium thiocyanate with H_2SO_4 in molecular proportions. The anhydrous acid is obtained by treating dry $Hg(CNS)_2$ with H_2S. Potassium thiocyanate is formed by fusing **KCN** with **S**. Or two parts of $K_4Fe(CN)_6$ with one part of sulphur. Also by fusing the cyanide or ferrocyanide of potassium with potassium thiosulphate, $K_2S_2O_3$:

$$2KCN + S_2 = 2KCNS$$
$$K_4Fe(CN)_6 + 3S_2 = 4KCNS + Fe(CNS)_2$$
$$4KCN + 4K_2S_2O_3 = 4KCNS + 3K_2SO_4 + K_2S$$
$$2K_4Fe(CN)_6 + 12K_2S_2O_3 = 12KCNS + 9K_2SO_4 + K_2S + 2FeS$$

Thiocyanic acid is quite as frequently called sulphocyanic acid, and its salts either thiocyanates or sulphocyanates. It corresponds to cyanic acid, **HCNO**, oxygen being substituted for sulphur.

Absolute thiocyanic acid, **HCNS**, is a colorless liquid, crystallizing at 12° and boiling at 85°. It has a pungent, acetous odor, and reddens litmus. It is soluble in water. The absolute acid decomposes quite rapidly at ordinary temperatures; the dilute solution slowly; with evolution of carbonic anhydride, carbon disulphide, hydrosulphuric acid, hydrocyanic acid, ammonia, and other products.

The same products result, in greater or less degree, from transposing *soluble* **thiocyanates** with strong acids; in greater degree as the acid is stronger and heat applied; while in dilute cold solution, the most of the thiocyanic acid remains undecomposed, giving the acetous odor. The thiocyanates, *insoluble* in water, are not all readily transposed. Thiocyanates of metals, whose sulphides are insoluble in certain acids, resist the action of the same acids.

The thiocyanates of the metals of the alkalis, alkaline earths; also, those of iron (ferrous and ferric), manganese, zinc, cobalt and copper—are **soluble in water.** Mercuric thiocyanate, sparingly soluble; potassium mercuric thiocyanate, more soluble. *Silver thiocyanate* is insoluble in water, insoluble in dilute nitric acid, slowly soluble in ammonium hydroxide.

Solutions of metallic **thiocyanates** give, with soluble salts of:

Cobalt, very concentrated, a blue color. $Co(CNS)_2$, crystallizable in blue needles, soluble in alcohol, not in carbon disulphide. The coloration is promoted by warming, and the test is best made in an evaporating dish. In strictly neutral solutions, iron, nickel, zinc and manganese, do not interfere.

Copper, if concentrated, a black crystalline precipitate, $Cu(CNS)_2$, soluble in thiocyanate. With **sulphurous acid**, a white precipitate, **CuCNS**; also with hydrosulphuric acid (used to separate a thiocyanate from a chloride) (Mann, *Z.*, 1889, **28**, 668).

Iron (ferrous), no precipitate or color.

Iron (ferric), an intensely blood-red solution of $Fe(CNS)_3$, decolored by solution of **mercuric chloride** (§126, 6*b*, *distinction from acetic acid*); decolored by phosphoric, arsenic, oxalic and iodic acids, etc., unless with excess of ferric salt; decolored by alkalis and by nitric acid, not by dilute hydrochloric acid. On introduction of metallic zinc, it evolves hydrosulphuric acid. Ferric thiocyanate is soluble in **ether**, which extracts traces of it from aqueous mixtures, rendering its color much more evident by the concentration in the ether layer.

Lead, gradually, a yellowish crystalline precipitate, $Pb(CNS)_2$, changed by boiling to white basic salt.

Mercury (mercurous), a white precipitate, **HgCNS**, resolved by boiling into **Hg** and $Hg(CNS)_2$. The mercurous thiocyanate, **HgCNS**, swells greatly *on ignition* (being used in "Pharaoh's serpents"), with evolution of **mercury, nitrogen, thiocyanogen, cyanogen** and sulphur dioxide.

Mercury (mercuric), in solutions not very dilute, a white precipitate, $Hg(CNS)_2$, somewhat soluble in excess of the thiocyanates, sparingly soluble in water, moderately soluble in alcohol. On ignition, it swells like the mercurous precipitate.

Platinum. Platinic chloride, gradually added to a hot, concentrated solution of potassium thiocyanate, forms a deep-red solution of double thiocyanate of potassium and platinum $(KCNS)_2Pt(CNS)_4$, or more properly, $K_2Pt(CNS)_6$, *potassium thiocyanoplatinate.* The latter salt gives bright-colored precipitates with metallic salts. The thiocyanoplatinate of lead (so formed) is golden-colored; that of silver, orange-red.

Silver, a white precipitate, $AgCNS$, insoluble in water, insoluble in dilute nitric acid, slowly soluble in ammonium hydroxide, readily soluble in excess of potassium thiocyanate; blackens in the light; soluble in hot concentrated H_2SO_4 (separation from $AgCl$) (Volhard, *A.*, 1877, **190**, 1).

Certain active oxidizing agents, viz., nascent chlorine, and nitric acid containing nitrogen oxides, acting in hot, concentrated solution of thiocyanates, precipitate *perthiocyanogen*, $H(CNS)_3$, of a yellow-red to rose-red color, even blue sometimes. It may be formed in the test for iodine, and mistaken for that element, in starch or carbon disulphide. If boiled with solution of potassium hydroxide, it forms thiocyanate.

Concentrated hydrochloric acid, or sulphuric acid, added in excess to water solution of thiocyanates, causes the gradual formation of a yellow precipitate, *perthiocyanic acid*, $(HCN)_2S_3$, slightly soluble in hot water, from which it crystallizes in yellow needles. It dissolves in alcohol and in ether.

Potassium thiocyanate can be fused in closed vessels, without decomposition; but with free access of air, it is resolved into sulphate and cyanate, with evolution of sulphurous acid.

When thiocyanic acid is oxidized, the final product, as far as the sulphur is concerned, is always sulphuric acid or a sulphate. In many cases (in acid mixture) it has been proven that the cyanogen is evolved as hydrocyanic acid. In other cases the same reaction is assumed as probable.

PbO_2 and Pb_3O_4 form Pb'' and sulphuric acid, in acid mixture only (Hardow, *J. C.*, 1859, **11**, 174).

H_3AsO_4 forms H_3AsO_3, hydrocyanic and sulphuric acids.

Co''' forms Co'', hydrocyanic and sulphuric acids.

Ni''' forms Ni'', hydrocyanic and sulphuric acids.

Cr^{VI} forms Cr''', hydrocyanic and sulphuric acids.

Mn''^{+n} forms Mn'', hydrocyanic and sulphuric acids. In alkaline mixture, a cyanate and sulphate are formed (Wurtz's *Dict. Chim.*, **3**, 95).

HNO_2 forms sulphuric acid and nitric oxide.

HNO_3 forms sulphuric acid and nitric oxide.

Cl forms at first a red compound of unknown composition, then HCl, H_2SO_4 and HCN are produced. In alkaline mixture a chloride and sulphate are formed.

$HClO$ same as with Cl.

$HClO_3$ forms sulphuric, hydrochloric and hydrocyanic acids.

Br forms HBr and H_2SO_4; but with alkalis, a bromide and sulphate.

$HBrO_3$ forms HBr and H_2SO_4.

HIO_3 forms H_2SO_4 and free iodine.

§235. Nitrogen. $N = 14.01$. Valence one to five (§11).

1. **Properties.**—Weight of molecule, N_2, 28.08. Vapor density, 14 (Jolly, *W. A.*, 1879, **6**, 536). At —123.8°, under pressure of 42.1 atmospheres, it condenses to a liquid (Sarrau, *C. r.*, 1882, **94**, 718). Boiling point, —194.4° (Olszewski, *W. A.*, 1897, **31**, 58). Liquid nitrogen is colorless and transparent. The gas is tasteless, odorless and colorless. Not poisonous, but kills by excluding air from the lungs. Does not burn or support combusion. It is very inert, not attacking other free elements. Its simplest combinations are the following: $N—'''H'_3$, N_2O, NO, N_2O_3, NO_2 and N_2O_5. The number of organic compounds containing nitrogen is very large. The nitrogen in all compounds that are the

immediate products of vegetable growth has a valence of minus three and may without change of bonds be converted into $N-'''H'_3$. This statement is made with a limited knowledge of the facts and without, at present, having conclusive proof; and merely predicting that future research will verify it.

2. **Occurrence.**—It constitutes about four-fifths of the volume of the atmosphere. It occurs as a nitrate in various salts and in various forms as a constituent of animal and vegetable growths.

3. **Formation.**—(*a*) From the air, the oxygen being removed by red-hot copper, the CO_2 by potassium hydroxide, the ammonia and water by passing through H_2SO_4.* (*b*) Ignition of ammonium dichromate, $(NH_4)_2Cr_2O_7 = N_2 + Cr_2O_3 + 4H_2O$. (*c*) By heating ammonium nitrate and peroxide of manganese to about 200° (Gatehouse, *C. N.*, 1877, **35**, 118). (*d*) Ignition of NH_4Cl and $K_2Cr_2O_7$: $2NH_4Cl + K_2Cr_2O_7 = 2KCl + N_2 + Cr_2O_3 + 4H_2O$. Unless the temperature be carefully guarded, traces of NO are formed, which may be removed by passing the gases through $FeSO_4$. (*e*) Action of chlorine upon NH_3: $8NH_3 + 3Cl_2 = 6NH_4Cl + N_2$. The NH_3 must be kept in excess to avoid the formation of the dangerously explosive chloride of nitrogen, NCl_3. (*f*) Removing the oxygen from the air by shaking with NH_4OH and copper turnings.* (*g*) Burning phosphorus in air over water.* (*h*) By passing air through a mixture of FeS and sawdust; then through a pyrogallate solution, and finally through concentrated H_2SO_4.* (*i*) By shaking air with $Fe(OH)_2$ and $Mn(OH)_2$.* (*j*) By passing air through an alkaline pyrogallate.* (*k*) By passing air, from which CO_2 has been removed, mixed with hydrogen over heated platinum black, the hydrogen having been added in just sufficient quantity to form water with all the oxygen * (Damoulin, *J.*, 1851, 321). (*l*) By warming a concentrated solution of NH_4NO_2 or a mixture of KNO_2 and NH_4Cl: $NH_4NO_2 = N_2 + 2H_2O$. Potassium dichromate is added to oxidize to nitric acid any of the oxides of nitrogen that may be formed (Gibbs, *B.*, 1877, 1387). (*m*) By action of potassium or sodium hypobromite upon ammonium chloride: $3NaBrO + 2NH_4Cl = N_2 + 3NaBr + 2HCl + 3H_2O$.

4. **Preparation.**—Nitrogen has been economically produced by most of the above methods.

5. **Solubilities.**—Nitrogen is nearly insoluble in all known liquids.

6. **Reactions.**—At ordinary temperatures nitrogen is not acted upon by other compounds. Nodules containing the so-called nitrifying bacteria growing on the roots of leguminous plants absorb nitrogen and build up nitrogenous compounds therewith.

7. **Ignition.**—Under electric influence it combines slowly with hydrogen; also with **B**, **Cr**, **Mg**, **Si** and **V**.

8. **Detection.**—Nitrogen is more easily detected by the nature of its compounds than by the properties of the liberated element.

9. **Estimation.**—(*a*) As free nitrogen by measuring the volume of the gas. (*b*) By oxidation of the organic substance with hot concentrated H_2SO_4, which also converts the nitrogen into ammonium sulphate. For details see works on organic analysis. (*c*) By decomposition of the organic material with potassium permanganate in strong alkaline solution, forming ammonia. (*d*) By combustion of the organic compound in presence of CuO and Cu, absorbing the CO_2 by KOH and determining the nitrogen by volume.

(For Hydroxylamine, see foot-note, page 286.)

§236. Hydrazoic acid (Azoimide). $N_3H = 43.038$.

Constitution,

Curtius, *B.*, 1890, **23**, 3023. A clear mobile liquid of penetrating odor, a very irritative effect upon the nostrils and the skin, and readily exploding with exceeding violence. Boiling point, about 37°. Soluble in water and alcohol. An acid of marked acidity, dissolving a number of metals with

* Nitrogen made from the air is not pure. It contains about one per cent of argon and smaller amounts of krypton, neon, and xenon. Because of the presence of these impurities its density is greater than that of nitrogen prepared from chemical compounds. (Ramsey and Rayleigh.)

evolution of hydrogen. Its salts, the trinitrides of the metals of the alkalis and the alkaline earths, are soluble in water and crystallizable (Dennis, *J. Am. Soc.*, 1898, **20**, 225). Potassium trinitride precipitates from thorium salts, the hydroxide of this metal in quantitative separation from cerium, lanthanum, neodymium and praseodymium (Dennis, *J. Am. Soc.*, 1896, **18**, 947). Hydronitric acid is formed by treating ammonia with sodium, and the resulting sodamide, $NaNH_2$, with nitrous oxide: $2NaNH_2 + N_2O = NaN_3 + NaOH + NH_3$ (Wislicenus, *B.*, 1892, **25**, 2084).

§237. Nitrous oxide. $N_2O = 44.02$.

$N'_2O^{-''}$, N — O — N.

Nitrous oxide becomes a colorless liquid at 0° under pressure of three atmospheres (Farady, *A.*, 1845, **56**, 157). Melts at —99° and boils at —92° (Wills, *J. C.*, 1874, **27**, 21). It is a colorless gas with slight sweetish smell and taste. Supports combustion. When breathed acts as an anæsthetic of short duration; and is used in dentistry for that purpose. Decomposed by heat completely at 900° into **N** and **O** (Meyer, *Pyrochemisch. Untersuch.*, 1885). Passed over red-hot iron **N** and Fe_2O_3 are formed. **K** and **Na** burn in nitrous oxide, liberating the nitrogen. As a rule both gases and solids that burn in air burn also in nitrous oxide. It is formed: (*a*) By heating ammonium nitrate in a retort from 170° to 260°: $NH_4NO_3 = N_2O + 2H_2O$. (*b*) By passing **NO** through solution of SO_2. (*c*) By action of HNO_3; *sp. gr.*, 1.42, diluted with an equal volume of water, upon metallic zinc. (*d*) A mixture of five parts of $SnCl_2$, ten parts of **HCl**, *sp. gr.*, 1.21, and nine parts of HNO_3, *sp. gr.*, 1.3, is heated to boiling: $2HNO_3 + 4SnCl_2 + 8HCl = 4SnCl_4 + N_2O + 5H_2O$ (Campari, *J. C.*, 1889, **55**, 569).

§238. Nitric oxide. NO = 30.01.

$N''O^{-''}$, N = O.

1. **Properties.**—The vapor density (15) shows the molecule to be **NO** (Daccomo and Meyer, *B.*, 1887, **20**, 1832). Under pressure of one atmosphere it is liquified at —153.6°, and under 71.2 atmospheres at —93.5°, and solidifies at —167° (Olszewski, *C. r.*, 1877, **85**, 1016). Odor and taste unknown, on account of its immediate conversion into NO_2 on exposure to the air.

2. **Occurrence.**—Not found free in nature.

3. **Formation.**—(*a*) Reduction of nitric acid by means of ferrous sulphate previously acidulated with H_2SO_4. (*b*) Action of cold nitric acid, *sp. gr.*, 1.2, upon metallic copper; unless great care be used other oxides of nitrogen are produced. (*c*) SO_2 is passed into slightly warmed HNO_3, *sp. gr.*, 1.15, and excess of SO_2 removed by passing through water. (*d*) According to Emich (*M.*, 1893, **18**, 73), a strictly pure nitric oxide is made by treating mercury with a mixture of nitric and sulphuric acids.

4. **Preparation.**—Same as above.

5. **Solubilities.**—Soluble in about ten volumes of water and in five volumes of nitric acid, *sp. gr.*, 1.3. One hundred volumes of H_2SO_4, *sp. gr.*, 1.84, and 1.50, dissolve 3.5 and 1.7 volumes respectively (Lunge, *B.*, 1885, **18**, 1391). A 16 per cent solution of ferrous sulphate dissolves six times its own volume of the gas forming the "brown ring," which is decomposed at 100°. Soluble in CS_2 and in alcohol.

6. **Reactions.**—When heated in nitric oxide to 450°, **Ag**, **Hg** and **Al** are unchanged; filings of **Cu**, **Fe**, **Cd** and **Zn** are superficially oxidized, but lead is completely changed to **PbO**; while if the metals are in an exceedingly fine state of division (by reduction of their oxides by hydrogen), **Ni** at 200° becomes **NiO**, **Fe** at 200° forms **FeO**, **Cu** at 200° forms Cu_2O; the higher oxides of these metals not being thus produced (Sabatier and Senderens, *C. r.*, 1892, **114**, 1429). Oxidized to KNO_3 by $KMnO_4$: $KMnO_4 + NO = MnO_2 + KNO_3$ (Wanklyn and Cooper, *Phil. Mag.*, 1878, (5), **6**, 288).

§239. Nitrous acid. $HNO_2 = 47.018$.

$$H'N'''O^{-''}_2, H - O - N = O.$$

1. **Properties.**—Nitrous acid is known only in solution. Made by adding N_2O_3 to water. It has a blue color and, owing to its tendency to dissociation ($6HNO_2 = 2HNO_3 + 4NO + 2H_2O$), is very unstable (Fremy, *C. r.*, 1870, **70**, 61). Nitrous anhydride is obtained when a mixture of one volume of oxygen and four volumes of nitric oxide are passed through a hot tube, $4NO + O_2 = 2N_2O_3$. It is a deep red gas, condensing to a blue liquid at 14.4° under 755 mm. pressure (Gains, *C. N.*, 1883, **48**, 97).

2. **Occurrence.**—Traces of ammonium nitrite are found in the air, in rain water, river water and in Chili saltpeter. When found in nature it is usually accompanied by nitrates.

3. **Formation.**—By action of nitric acid, *sp. gr.*, 1.35, upon starch or arsenous oxide. At 70° nearly pure N_2O_3 is obtained, which passed into cold water forms HNO_2. Nitrites of potassium and sodium may be formed by ignition of their nitrates (a prolonged high heat forming the oxides). Or the alkali nitrites may be made by fusing the nitrates with finely divided iron; lead nitrite by fusing lead nitrate with metallic lead, and silver nitrite may be made from these by precipitation; and from this salt many nitrites may be made nearly pure by transposition; *e. g.*, $BaCl_2 + 2AgNO_2 = Ba(NO_2)_2 + 2AgCl$ and then $Ba(NO_2)_2 + ZnSO_4 = Zn(NO_2)_2 + BaSO_4$.

4. **Preparation.**—Same as above.

5. **Solubilities.** Silver nitrite is only sparingly soluble (120 parts of cold water). The other normal nitrites are soluble; but many basic nitrites are insoluble.

Nascent hydrogen in presence of an alkali reduces nitrates to nitrites; *e. g.*, sodium amalgam, aluminum wire in hot **KOH**, etc. Used in excess the nascent hydrogen reduces the nitrogen still further, forming NH_3.

6. **Reactions.**—*A.*—**With metals and their compounds.**—Nitrous acid acts sometimes as an oxidizer, sometimes as a reducer; in the former case **NO** is *usually* produced (under some conditions N_2O, **N** and NH_3 are formed); in the latter case nitric acid is the usual product, but sometimes NO_2 is produced.

1. PbO_2 becomes Pb'' and nitric acid.

2. Hg' becomes Hg° and nitric acid.

3. Cr^{VI} becomes Cr''' and nitric acid.

4. Co'' becomes Co''' and nitric oxide. Excess of KNO_2 with acetic acid is used to separate cobalt from nickel (§**132**, 6*c*).

5. Ni''' becomes Ni'' and nitric acid.

6. $Mn'' + n$ becomes Mn'' and nitric acid.

B.—**With non-metals and their compounds.**—

1. $H_4Fe(CN)_6$ becomes first $H_3Fe(CN)_6$ and then hydronitroferricyanic acid. Solution of indigo in sulphuric acid is bleached by nitrites.

2. Nitrites are decomposed by nitric acid.

3. HH_2PO_2 becomes H_3PO_4 and **NO**.

4. H_2S does not displace or transpose alkali nitrites, but if acetic acid be added to liberate the nitrous acid, then S° and **NO** are produced. H_2SO_3 becomes H_2SO_4 and chiefly **NO**. With excess of H_2SO_3, N_2O or NH_3 is formed. See Weber, *Pogg.*, 1866, **127**, 543, and 1867, **130**, 277; Fremy, *C. r.*, 1870, **70**, 61.

5. $HClO_3$ becomes Cl° and HNO_3.

6. $HBrO_3$ becomes Br° and HNO_3

7. **HI** becomes I° and **NO**.
HIO_3 becomes I° and HNO_3.

7. **Ignition.** In general nitrites are changed to oxides, but with potassium and sodium nitrites a white heat is required, and with nitrites of **Ag**, **Hg**, **Au** and **Pt** the dissociation goes a step further, the free metals being produced.

8. **Detection.**—(*1*) Formation of brown ring when ferrous sulphate solution and a nitrite is acidulated with acetic acid. Nitrates require a stronger acid for

their transposition. (*2*) A mixture of a nitrite and **KI** liberates iodine on addition of acetic acid (nitrates requiring a stronger acid for transposition). (*3*) Nitrous acid with iodic acid liberates iodine, and nitric acid is produced. (*4*) Solution of potassium permanganate acidified with sulphuric acid is reduced by nitrites (distinction from nitrates).

9. **Estimation.**—Acidify with acetic acid, distil and titrate the distillate with standard solution of permanganate.

§240. Nitrogen peroxide (dioxide). $NO_2 = 46.01$.

Vapor density, 23 (Ramsay, *J. C.*, 1890, **57**, 590). Melting point, —10° (Deville and Troost, *C. r.*, 1867, **64**, 257). Boils at 21.64° (Thorpe, *J. C.*, 1880, **37**, 224). Below —10° it is a white crystalline solid. Between —10° and 21.64° a liquid; nearly colorless at —9°, yellow at 0°. At 21.64°, orange, growing nearly black as the temperature rises. The gas does not support combustion of ordinary fuels, and is poisonous when inhaled. It dissolves in water, forming a greenish-blue solution containing nitrous and nitric acids. With an aqueous solution of a fixed alkali a nitrate and nitrite are formed: $2NO_2 + 2KOH = KNO_2 + KNO_3 + H_2O$.

§241. Nitric acid. $HNO_3 = 63.018$.

$$H'N^{V}O^{-''}{}_3, \quad H-O-\overset{\overset{O}{\|}}{N}=O.$$

1. **Properties.**—Nitric anhydride, N_2O_5, is a colorless solid, melting at 30° with partial decomposition to NO_2 and **O**, and if exposed to direct sunlight decomposition begins at lower temperatures.

Nitric acid, HNO_3, has not been perfectly isolated; that containing 99.8 per cent of HNO_3 is a colorless highly corrosive liquid (Roscoe, *A.*, 1860, **116**, 211), solidifies at 47° (Berthelot), boils at 86°, but dissociation begins at a lower temperature and is complete at 255°: $4HNO_3 = 4NO_2 + 2H_2O + O_2$ (Carius, *B.*, 1871, **4**, 828). If the very dilute acid be boiled, it becomes stronger, and if a very strong acid be boiled it becomes weaker, in both cases a *sp. gr.* of 1.42 and boiling point of 120° being reached; the acid then contains about 70 per cent of HNO_3 (Kolbe, *A. Ch.*, 1867, (4), **10**, 136). This is the acid usually placed on the market. The reagent usually employed has a *sp. gr.* of 1.2 (Fresenius standard). The so-called fuming acid has a specific gravity of 1.50 to 1.52. The stronger acid should be kept in a cool dark place to avoid decomposition.

2. **Occurrence.**—Found in nature as nitrates of **K**, **Na**, NH_4, **Ca**, **Mg**, and of a few other metals, the most abundant supply coming from Chili and Bolivia as sodium nitrate, "Chili saltpeter."

3. **Formation.**—(*a*) Oxidation of nitrogenous matter in presence of air, moisture and an oxide or alkali; (*b*) by oxidation of **NO**, N_2O_3 or NO_2 by oxygen (or air) in presence of moisture; (*c*) from NH_3, by passing a mixture of NH_3 and oxygen through red-hot tubes.

4. **Preparation.**—By treating nitrates with sulphuric acid and distilling.

Nitrates may be made: (*a*) By dissolving the metal in nitric acid, except those whose metals are not attacked by that acid, *e. g.*, **Au**, **Pt**, **Al** and **Cr**; and also, antimony forms Sb_2O_5, arsenic, H_3AsO_4 and with excess of hot acid tin forms metastannic acid $H_{10}Sn_5O_{15}$. (*b*) By adding HNO_3 to the oxides, hydroxides or carbonates. All the known nitrates can be made

in this manner. (*c*) By long continued boiling, the chlorides of all ordinary metals are completely decomposed, no chlorine remaining, except the chlorides of **Hg**, **Ag**, **Au** and **Pt**, which are not attacked, and the chlorides of tin and antimony, which are changed to oxides. (Wurtz, *Am. S.*, 1858, **75**, 371; Johnson, *Proc. Am. Ass. Sci.*, 1894, 163.)

The anhydride is made: (*a*) By passing chlorine over silver nitrate: $4AgNO_3 + 2Cl_2 = 4AgCl + 2N_2O_5 + O_2$. (*b*) By adding anhydrous P_2O_5 to HNO_3: $2NHO_3 + P_2O_5 = 2HPO_3 + N_2O_5$.

5. **Solubilities.**—All normal nitrates are soluble. A few are decomposed by water, *e. g.*, $Bi(NO_3)_3 + H_2O = BiONO_3 + 2HNO_3$. Most nitrates are less soluble in nitric acid than in water. *e. g.*, **Cd**, **Pb**, **Ba**, etc.; the barium nitrate being completely insoluble in HNO_3, *sp. gr.*, 1.42.

Nitric acid decomposes the sulphides of all ordinary metals, except mercuric sulphide which by long continued boiling with the concentrated acid becomes $2HgS.Hg(NO_3)_2$, insoluble in the acid.

6. **Reactions.** *A.*—**With metals and their compounds.**—Nitric acid is a powerful oxidizer but unless warmed acts more slowly than chlorine. It can never be a reducer. The following products are formed: **H**, NH_3, H_2NOH *, **N**, N_2O, **NO**, HNO_2, NO_2. If the acid is concentrated, in excess and hot, the product is usually entirely nitric oxide, colorless, but changing to the red colored NO_2 by coming in contact with the air. Excess of the reducer, low temperatures and dilute solutions favor the production of nitrogen compounds having lower valence and of hydrogen. Nascent hydrogen usually forms NH_3, always the ultimate product if the hydrogen be produced in alkaline mixture.

Nitric acid oxidizes all ordinary metals. (It does not act upon chromium, gold or platinum.) It forms nitrates, except in the case of tin, antimony, and arsenic, with which it forms $H_{10}Sn_5O_{15}$, Sb_2O_5, and H_3AsO_4. With the respective metals it forms **Hg**′ or **Hg**″, **Sn**″ or **Sn**⁗, **As**‴ or **As**^{V}, **Sb**‴ or **Sb**^{V}, **Fe**″ or **Fe**‴, according to the amount of nitric acid employed. With copper it forms cupric nitrate (never cuprous); with cobalt it forms cobaltous nitrate.

* Hydroxylamine, NH_2OH, is formed by the reducing action of **Sn** and **HCl** upon **NO**, N_2O_3, HNO_3, etc. (Lossen, *A.*, 1888, **252**, 170); also by the action of H_2S, SO_2, **K**, **Na**, **Mg**, **Zn**, and **Al** upon HNO_3, or by the action of H_2S upon certain nitrates (Divers and Haga, *C. N.*, 1886, **54**, 271). By action of sodium amalgam upon sodium nitrite solution, NH_2OH is produced along with nitrous oxide, free nitrogen, ammonia, sodium hyponitrite, and sodium hydroxide, the highest yield of the hydroxylamine being obtained when the nitrite solution is as dilute as one in fifty, the mixture being kept cold (Divers, *J. C.*, 1899, **75**, 87 and 89). It is a base with an alkaline reaction and is a strong reducing agent. When pure it is a crystalline solid, odorless, melting at 33.05°, boiling at 58° at 22 mm. pressure; oxidized by oxygen to HNO_2 (Lobry de Bruyn, *B.*, 1892, **25**, 3, 190 and 684). It is a good antiseptic and preservative. It combines with acids to form salts: $NH_2OH + HCl = NH_2OH.HCl$. Hydroxylamine hydrochloride is decomposed by alkalis forming the free base, which is decomposed by the halogens, $KMnO_4$, $K_2Cr_2O_7$, BaO_2 and PbO_2. Its solution in ether reacts with sodium, forming a white precipitate of NH_2ONa.

1. PbO_2 is not changed. Pb_3O_4 is changed thus: $Pb_3O_4 + 4HNO_3 = PbO_2 + 2Pb(NO_3)_2 + 2H_2O$.

2. Hg' becomes Hg''.

3. Sn'' becomes Sn^{IV}. **Stannous chloride and hydrochloric acid,** heated with a nitrate, form stannic chloride, and convert nitric acid to *ammonia* (which remains as ammonium salt). See §71, 6*c*.

4. Sb''' becomes Sb^{V}, forming Sb_2O_5, insoluble.

5. As''' becomes As^{V}, forming H_3AsO_4.

6. Cu' becomes Cu''.

7. Fe'' becomes Fe'''.

B.—**With non-metals and their compounds.**

1. Carbon (ordinary, not graphite) becomes CO_2 if the nitric acid be hot and concentrated.

$H_2C_2O_4$ becomes CO_2, in hot concentrated acid.

$H_4Fe(CN)_6$ becomes first $H_3Fe(CN)_6$ and then hydronitroferricyanic acid.

$HCNS$ is oxidized, the sulphur becoming H_2SO_4.

2. Nitrites are all decomposed, nitrates being formed, the nitric acid not being reduced. The nitrous acid liberated immediately dissociates: $3HNO_2 = 2NO + HNO_3 + H_2O$.

3. $P°$, PH_3, HH_2PO_2 and H_3PO_3 become H_3PO_4. That is P^{V-n} becomes P^{V}.

4. S becomes H_2SO_4.

H_2S becomes first $S°$ and then H_2SO_4.

H_2SO_3 becomes H_2SO_4 ; and in general S^{VI-n} becomes S^{VI}.

$$2HNO_3 + 3H_2SO_3 = 2NO + 3H_2SO_4 + H_2O.$$

5. HCl, nitrohydrochloric acid: $2HNO_3 + 6HCl = 2NO + 4H_2O + 3Cl_2$ (Koninck and Nihoul, *Z. anorg.*, 1890, 477). See §269, 6*B2*.

$HClO_3$ is not reduced. Chlorates are all transposed but not decomposed until the temperature and degree of concentration is reached that would dissociate the $HClO_3$ if the nitric acid were absent.

6. $Br°$ is not oxidized. HBr becomes $Br°$ and is not further oxidized. All bromates are transposed but the $HBrO_3$ is not decomposed until a temperature and degree of concentration is reached that would cause the dissociation of the $HBrO_3$ if the nitric acid were absent.

7. $I°$ becomes HIO_3, very slowly unless the fuming acid be used.

HI becomes first $I°$; then as above.

$$2HNO_3 + 6HI\text{, excess} = 2NO + 3I_2 + H_2O$$
$$HI + HNO_3\text{, excess} = 2NO + HIO_3 + H_2O$$

8. In general, organic compounds are oxidized. Straw, hay, cotton, etc., are inflamed by the strong acid (Kraut, *B.*, 1881, **14**, 301). For action on starch, see Lunge, *B.*, 1878, **11**, 1229, 1641. With many organic bodies

substitution products are formed, the oxides of nitrogen taking the place of the hydrogen.

7. **Ignition.**—Nitric acid is dissociated by heat: $4HNO_3 = 4NO_2 + 2H_2O + O_2$, complete if at 256° (Carius, *B.*, 1871, **4**, 828). No nitrates are volatile as such. Ammonium nitrate is dissociated: $NH_4NO_3 = N_2O + 2H_2O$. Some nitrates, *e. g.*, those of **K** and **Na**, are first changed to nitrites with evolution of oxygen only, and at an intense white heat further changed to oxides with evolution of N_2O as well as oxygen. As a final result of ignition the nitrates of all ordinary metals are left as oxides, except that those of **Hg**, **Ag**, **Au** and **Pt** are reduced to the free metal.

A mixture of potassium nitrate and sodium carbonate in a state of fusion is a powerful oxidizer; *e. g.*, changing Sn'' to Sn^{IV}, As''' to As^{V}, Sb''' to Sb^{V}, Fe'' to Fe''', Cr''' to Cr^{VI}, Mn^{VI-n} to Mn^{VI}, S^{VI-n} to S^{VI}, etc.

Heated on charcoal, or with potassium cyanide, or sugar, sulphur or other easily oxidizable substance (as in gunpowder), nitrates are reduced with *deflagration or explosion*, more or less violent. With potassium cyanide, on platinum foil, the deflagration is especially vivid. In this reaction free *nitrogen* is evolved.

Strongly heated with excess of potassium hydroxide and sugar or other carbonaceous compound, in a dry mixture, nitrates are reduced to *ammonia*, which is evolved, and may be detected. In this carbonaceous mixture, the nitrogen of nitrates reacts with alkalis, like the unoxidized nitrogen in carbonaceous compounds.

8. **Detection.**—Most of the tests for the **identification** of nitric acid are made by its deoxidation, disengaging a lower oxide of nitrogen, or even, by complete deoxidation, forming ammonia.

If, with concentrated sulphuric acid, a bit of **copper** turning, or a crystal of ferrous sulphate, is added to a concentrated solution or residue of nitrate, the mixture gives off abundant brown vapors: the colorless *nitric oxide*, **NO**, which is set free from the mixture, oxidizing immediately in the air to nitrogen peroxide, NO_2:

$$2KNO_3 + 4H_2SO_4 + 3Cu = K_2SO_4 + 3CuSO_4 + 4H_2O + 2NO$$
$$2KNO_3 + 4H_2SO_4 + 6FeSO_4 = K_2SO_4 + 3Fe_2(SO_4)_3 + 4H_2O + 2NO$$

The *three atoms of oxygen furnished by two molecules of nitrate* suffice to oxidize three atoms of copper; so that $3CuO$ with $3H_2SO_4$, may form $3CuSO_4$ and $3H_2O$. The same three atoms of oxygen (having six bonds) suffice to oxidize six molecules of ferrous salt into three molecules of ferric salt; so that $6FeSO_4$ with $3H_2SO_4$, can form $3Fe_2(SO_4)_3$ and $3H_2O$.

Now if, by the last-named reaction, the nitric oxide is disengaged in cold solution, with excess of ferrous salt and of sulphuric acid, instead of passing off, the nitric oxide combines with the ferrous salt, forming a *black-brown liquid*, $(FeSO_4)_2NO$, decomposed by heat and otherwise unstable: $2KNO_3 + 4H_2SO_4 + 10FeSO_4 = K_2SO_4 + 3Fe_2(SO_4)_3 + 4H_2O + 2(FeSO_4)_2NO$.

a.—This exceedingly delicate "**Brown ring**" test for nitric acid or nitrates in solution may be conducted as follows: If the solution of a nitrate is mixed with an equal volume of concentrated H_2SO_4, the mixture

allowed to cool and a concentrated solution of $FeSO_4$ then cautiously added to it, so that the fluids do not mix, the junction shows at first a purple, afterwards a brown color (Fresenius, *Qual. Anal.*, *16th ed.*, 387). A *second* method of obtaining the same brown ring is: Take sulphuric acid to a quarter of an inch in depth in the test-tube; add without shaking a nearly equal bulk of a solution of ferrous sulphate, cool; then add slowly of the solution to be tested for nitric acid, slightly tapping the test-tube on the side but not shaking it. The brown ring forms between the two layers of the liquid. A *third* method often preferred is: Take ferrous sulphate solution to half an inch in depth in the test-tube; add two or three drops of the liquid under examination and mix thoroughly; incline the test-tube and add an equal volume of concentrated H_2SO_4 in such a way that it will pass to the bottom and form a separate layer. Cool and let it stand a few minutes without shaking. Nitrous acid interferes with this test but the brown ring is produced when a nitrite is acidified with acetic acid while sulphuric acid is required in the case of a nitrate (§**239**, 8). If the presence of a nitrite is suspected, the solution should first be acidified with acetic acid and ferrous sulphate added. If a brown color is produced a nitrite is present. The nitrite may be removed by boiling the solution until the brown color has disappeared and does not return on adding more ferrous sulphate solution and acetic acid. After cooling the solution, a nitrate may be tested for by means of strong sulphuric acid and ferrous sulphate.

If strong oxidizing agents are present, excess of $FeSO_4$ should be added and the solution warmed. The solution should be cooled before applying the test. Metals forming insoluble sulphates should be removed by adding Na_2CO_3 and warming. Iodides interfere by forming a brown ring of free iodine.

b.—**Indigo solution.**—In presence of **HCl** heat moderately and the blue color is destroyed. Interfering substances, $HClO_3$, HIO_3, $HBrO_3$, Fe''', Cr^{VI}, Mn^{VII}, and all that convert **HCl** into Cl_2.

c.—**Sodium salicylate** is added to the solution, H_2SO_4 is slowly added, the test-tube being inclined. Avoid shaking, keep cool for five minutes. A yellow ring indicates HNO_3. To increase the brilliancy of the color, shake, cool and add to HN_4OH.

d.—**Ammonium test.**—Treat the solution with **KOH** and **Al** wire, warm until gas is evolved. Pass the gas into water containing a few drops of Nessler's reagent. A yellowish-brown precipitate indicates HNO_3: $3HNO_3 + 8Al + 8KOH = 3NH_3 + 8KAlO_2 + H_2O$. Nothing interferes with this test, but action is delayed by Cl^V, I^V and many other oxidisers. Ammonia and ammonium salts must be removed by evaporation with **NaOH** before applying the test.

e.—**Nitrite test.**—Reduce the nitrate to nitrite by warming with **Al** and **KOH**. At short intervals decant a portion of the solution, add a drop of **KI**, acidify with $HC_2H_3O_2$ and test for **I** with CS_2. This test should always be made in connection with (*d*). Other oxidisers including Cl^V, Br^V, I^V, and As^V are reduced before the reduction of the HNO_3 begins:

$$3HNO_3 + 2Al + 5KOH = 3KNO_2 + 2KAlO_2 + 4H_2O$$
$$2KNO_2 + 2KI + 4HC_2H_3O_2 = I_2 + 4KC_2H_3O_2 + 2H_2O + 2NO$$

Other means of making the nascent hydrogen are sometimes preferred; *e. g.*, sodium amalgam, a mixture of **Zn** and **Fe** both finely divided and used with excess of hot **KOH**, or finely divided **Mg** in presence of H_3PO_4.

f. Various organic compounds give characteristic color reactions with nitric acid. An excellent reagent of this kind consists of a solution of **dimethyl aniline** (2 drops) and **p-toluidine** (0.2 grams) in 50% sulphuric acid (10 c.c.). A blood red color is produced when this reagent is brought into contact with even a dilute solution of a nitrate. The color appears as a ring test between the two liquids. Reducing agents especially ferrous salts interfere with the test. By the addition of a crystal of $KClO_3$ and **HCl** and boiling, the interference may be overcome. $KClO_3$ gives a brown color but on dilution the red color of the nitrate generally appears. $KClO_3$ may be removed by heating with **HCl**. (Woodruff, *J. Am. Soc.* **19**, 156. Schmidt and Lump (Ber. **43**, 794) also give a color reagent which gives a red color. The reagent is a solution of 0.1 gram of **Di-9,10-monoxyphenanthrylamine** in 1000 c.c. conc. H_2SO_4. The dry salt or the residue obtained by evaporation of the unknown solution is added to a few c.c. of the blue reagent which turns red in the presence of a nitrate. Oxidizing agents do not interfere.

Add three drops of the solution to be tested to two drops of **diphenylamine**, $(C_6H_5)_2NH$, dissolved in H_2SO_4. A blue color indicates a nitrate. Cl°, Cl^V, Br^V, I^V, Mn^{VII}, Cr^{VI}, Se^{IV}, and Fe''' interfere with this test. This test is of especial value in showing the absence of nitrates. If no color is obtained, it is certain that no nitrate is present.

g.—**Brucine,** dissolved in concentrated sulphuric acid, treated (on a porcelain surface) with even traces of nitrates, gives a fine deep-red color, soon paling to reddish-yellow. If now stannous chloride, dilute solution, be added, a fine red-violet color appears. (Chloric acid gives the same reaction.)

h.—**Phenol,** C_6H_5OH, gives a deep red-brown color with nitric acid, by formation of nitrophenol (mono, di or tri), $C_6H_4(NO_2)OH$ to $C_6H_2(NO_2)_3OH$, "picric acid" or nitrophenic acid. A mixture of one part of phenol (cryst. carbolic acid), four parts of strong sulphuric acid, and two parts of water, constitutes a reagent for a very delicate test for nitrates (or nitrites), a few drops being sufficient. With unmixed nitrates the action is explosive, unless upon very small quantities. The addition of potassium hydroxide deepens and brightens the color. According to Sprengel (*J. C.*, 1863, **16**, 396), the somewhat similar color given by compounds of chlorine, bromine, iodine and by organic matter may be removed by adding ammonium hydroxide without diminishing the brightness of the color formed by the nitrates.

i.—According to Lindo (*C. N.*, 1888, **58**, 176), **resorcinal** is five times more delicate a test than phenol. Ten grammes of resorcinol are dissolved in 100 cc. of water; one drop of this solution with one drop of a 15 per cent solution of **HCl** and two drops of concentrated H_2SO_4 are added to 0.5 cc. of the nitrate to be tested. Nitrous acid gives the same purple color.

j.—A little **pyrogallol** is dissolved in the liquid to be tested (less than one mg. to one cc.) and ten drops of concentrated H_2SO_4 are dropped down the side of the test tube so as to form two layers; at the surface of contact a brown or yellow coloration appears if nitric acid is present. One mg. of nitric acid in one litre of potable water can thus be detected (Curtman, *Arch. Pharm.*, 1886, **223**, 711).

9. **Estimation.**—(*a*) If the base is one capable of readily forming a silicate, the nitrate is fused with SiO_2 and estimated by the difference in weight. (*b*) By treating with hot sulphuric acid, passing the distillate into $BaCO_3$ and estimating the nitric acid by the amount of barium dissolved. (*c*) Treating with **Al** and **KOH** and estimating the distillate as NH_3. (*d*) Neutralizing the free acid with ammonium hydroxide, and after evaporation and drying at 115°, weighing as ammonium nitrate. (*e*) In presence of free H_2SO_4 a ferrous solution of known strength is added in excess to the nitrate and the amount of ferrous salt remaining is determined by a standard solution of potassium permanganate. (*f*) The volume of hydrogen generated by the action of potassium hydroxide upon a known quantity of aluminum is measured; and the test is then repeated under the same conditions, but in presence of the nitrate. The difference in the volume of the hydrogen obtained represents the quantity of NH_3 that has been formed.

§242. Oxygen. O = 16.000. Usual valence two.

1. **Properties.**—A colorless, odorless gas; *specific gravity*, 1.10535 (Rayleigh, *Proc. Roy. Soc.*, 1897, 204). When heated it diffuses through silver tubing quite rapidly (Troost, *C. r.*, 1884, **98**, 1427). It may be liquefied by cooling the gas under great pressure and then suddenly allowing it to expand under reduced pressure. It *boils* at − 113° under 50 atmospheres pressure; and at − 184° under one atmosphere pressure (Wroblewski, *C. r.*, 1884, **98**, 304 and 982). Its *critical temperature* is about − 118.8°, and the *critical pressure* 50.8 atmospheres. *Specific gravity* of the liquid at − 181.4°, 1.124 (Olszewski, *M.*, 1887, 8, 73). Oxygen is sparingly soluble in water with a slight increase in the volume (Winkler, *B.*, 1889, **22**, 1764); slightly soluble in alcohol (Carius, *A.*, 1855, **94**, 134). Molten silver absorbs about ten volumes of oxygen, giving it up upon cooling (blossoming of silver beads) (Levol, *C. r.*, 1852, **35**, 63). It transmits sound better than air (Bender, *B.*, 1873, **6**, 665). It is not combustible, but supports combustion much better than air. In an atmosphere of oxygen, a glowing splinter bursts into a flame; phosphorus burns with vivid incandescence; also an iron watch spring heated with burning sulphur. It is the most negative of all the elements except fluorine; it combines directly or indirectly with all the elements except fluorine; with the alkali metals rapidly at ordinary temperature. The combination of oxygen with elements or compounds is termed combustion or oxidation. The temperature at which the combination takes place varies greatly: phosphorus at 60°; hydrogen in air at 552°; in pure oxygen at 530° (Mallard and Le Chatelier, *Bl.*, 1883, (2), **39**, 2); carbon disulphide at 149°; carbon at a red heat; while the halogens do not combine by heat alone.

2. **Occurrence.**—The rocks, clay and sand constituting the main part of the earth's crust contain from 44 to 48 per cent of oxygen; and as water contains 88.81 per cent, it has been estimated that one-half of the crust is oxygen. Except in atmospheric air, which contains about 23 per cent of uncombined oxygen, it is always found combined.

3. **Formation.**—(*a*) By igniting HgO. (*b*) By heating $KClO_3$ to 350°, $KClO_4$ is produced and oxygen is evolved; at a higher temperature the $KClO_4$ becomes KCl. In the presence of MnO_2 the $KClO_3$ is completely changed to KCl at 200°, without forming $KClO_4$, the MnO_2 not being changed. Spongy platinum, CuO, Fe_2O_3, PbO_2, etc., may be substituted for MnO_2 (Mills and Donald, *J. C.*, 1882, **41**, 18; Boudrimont, *Am. S.*, 1872, **103**, 370). Spongy platinum, ruthenium,

rhodium and indium with chlorine water or with hydrogen peroxide evolve oxygen. The spongy ruthenium acts most energetically (Schoenbein, *A. Ch.*, 1866, (4), **7**, 103). (*c*) Action of heat on similar salts furnishes oxygen; *e. g.*, $KClO$ and $KClO_2$ form KCl, $KBrO_3$ forms KBr, KIO_3 and KIO_4 form KI, and KNO_3 forms KNO_2 (at a white heat K_2O, NO and O are formed). (*d*) By the action of heat on metallic oxides as shown in the equations below. (*e*) By heating higher oxides or their salts with sulphuric acid. Cr^{VI} is changed to Cr''', Co''' to Co'', Ni''' to Ni'', Bi^{V} to Bi''', Fe^{VI} to Fe''', Pb^{IV} to Pb'', and Mn''^{+n} to Mn''; in each case a sulphate is formed and oxygen given off:

a. $2HgO$ (at 500°) $= 2Hg + O_2$

b. $10KClO_3$ (at 350°) $= 6KClO_4 + 4KCl + 3O_2$ (Teed, *J. C.*, 1887, **51**, 283)

$2KClO_3$ (at red heat) $= 2KCl + 3O_2$

$2KClO_3 + nMnO_2$ (at 200°) $= nMnO_2 + 2KCl + 3O_2$

c. $KClO_2 = KCl + O_2$

$2KBrO_3 = 2KBr + 3O_2$

$2KIO_3 = 2KI + 3O_2$

$KIO_4 = KI + 2O_2$

$2KNO_3 = 2KNO_2 + O_2$

$4KNO_2$ (white heat) $= 2K_2O + 4NO + O_2$

d. $2Pb_3O_4$ (white heat) $= 6PbO + O_2$

$2Sb_2O_5$ (red heat) $= 2Sb_2O_4 + O_2$

Bi_2O_5 (red heat) $= Bi_2O_3 + O_2$

$4CrO_3$ (about 200°) $= 2Cr_2O_3 + 3O_2$

$4K_2Cr_2O_7$ (red heat) $= 2Cr_2O_3 + 4K_2CrO_4 + 3O_2$

$6Fe_2O_3$ (white heat) $= 4Fe_3O_4 + O_2$

$3MnO_2$ (white heat) $= Mn_3O_4 + O_2$

$6Co_2O_3$ (dull-red heat) $= 4Co_3O_4 + O_2$

$2Ni_2O_3$ (dull-red heat) $= 4NiO + O_2$

$2Ag_2O$ (300°) $= 4Ag + O_2$

$2BaO_2$ (800°) $= 2BaO + O_2$

e. $2K_2Cr_2O_7 + 8H_2SO_4 = 4KCr(SO_4)_2 + 3O_2 + 8H_2O$

$4KMnO_4 + 6H_2SO_4 = 2K_2SO_4 + 4MnSO_4 + 5O_2 + 6H_2O$

$2Pb_3O_4 + 6H_2SO_4 = 6PbSO_4 + 6H_2O + O_2$

4. **Preparation.**—(*a*) By heating $KClO_3$ to 200° in closed retorts in the presence of MnO_2 or Fe_2O_3. If $KClO_3$ be heated alone, higher heat (350°) is required, and the gas is given off with explosive violence. About equal parts of the metallic oxide and $KClO_3$ should be taken. (*b*) BaO heated in the air to 550° becomes BaO_2, and at 800° is decomposed into BaO and O, making theoretically a cheap process. (*c*) By heating calcium plumbate. The calcium plumbate is regenerated by heating in the air (Kassner, *J. C.*, 1894, **66**, ii, 89). (*d*) By passing sulphuric acid over red-hot bricks: $2H_2SO_4 = 2SO_2 + 2H_2O + O_2$; the SO_2 is separated by water, and after conversion into H_2SO_4 (§266, 4) is used over again. (*e*) By warming a saturated solution of chloride of lime with a small amount of cobaltic oxide, freshly prepared and moist. The cobaltic oxide seems to play the same rôle as NO in making H_2SO_4 (Fleitmann, *A. Ch.*, 1865, (4), **5**, 507). (*f*) The following cheap process is now employed on a *large scale*. Steam is passed over sodium manganate at a dull-red heat; Mn_2O_3 and oxygen are formed. Then, without change of apparatus or temperature, air instead of steam is passed over the mixture of Mn_2O_3 and $NaOH$. The Mn_2O_3 is thus again oxidized to Na_2MnO_4, and free nitrogen is liberated:

$4Na_2MnO_4 + 4H_2O$ (dull-red heat) $= 8NaOH + 2Mn_2O_3 + 3O_2$

$8NaOH + 2Mn_2O_3 +$ air, $3(O_2 + 4N_2) = 4Na_2MnO_4 + 4H_2O + 12N_2$

5. **Solubilities.**—See 1.

6. **Reactions.**—Pure oxygen may be breathed for a short time without injury. A rabbit placed in pure oxygen at 24° lived for three weeks, eating voraciously

all the time, but nevertheless becoming thin. The action of oxygen at 7.2° is to produce narcotism and eventually death. When oxygen is cooled by a freezing mixture it induces so intense a narcotism that operations may be performed under its influence. Compressed oxygen is "the most fearful poison known." The pure gas at a pressure of 3.5 atmospheres, or air at a pressure of 22 atmospheres, produces violent convulsions, simulating those of strychnia poisoning, ultimately causing death. The arterial blood in these cases is found to contain about twice the quantity of its normal oxygen. Further, compressed oxygen stops fermentation, and permanently destroys the power of yeast.

At varying temperatures oxygen combines directly with all metals except silver, gold and platinum, and with these it may be made to combine by precipitation. It combines with all non-metals except fluorine; the combination occurring directly, at high temperatures, except with **Cl**, **Br** and **I**, which require the intervention of a third body.

7. **Ignition.**—Most elements when ignited with oxygen combine readily. Some lower oxides combine with oxygen to form higher oxides, and certain other oxides evolve oxygen, forming elements or lower oxides. Oxides of gold, platinum and silver cannot be formed by igniting the metals in oxygen; they must be formed by precipitation.

8. **Detection.**—Uncombined oxygen is detected by its absorption by an alkaline solution of pyrogallol; by the combination with indigo white to form indigo blue; by its combination with colorless **NO** to form the brown NO_2; by its combination with phosphorus, etc. It is separated from other gases by its absorption by a solution of chromous chloride, pyrogallol or by phosphorus. In combination in certain compounds it is liberated in whole or in part by simple ignition; as with $KClO_3$, $KMnO_4$, HgO, Au_2O_3, PtO_2, Ag_2O, Sb_2O_5, etc. In other combinations by ignition with hydrogen, forming water.

9. **Estimation.**—Free oxygen is usually estimated by bringing the gases in contact with phosphorus or with an alkaline solution of pyrogallol (CO_2 having been previously removed), and noting the dimunition in volume. Oxygen in combination is usually estimated by difference.

§243. Ozone. $O_3 = 48.000$.

Ozone was first noticed by Van Marum in 1785 as a peculiar smelling gas formed during the electric discharge; and which destroyed the lustre of mercury. Schoenbein (*Pogg.*, 1840, **50**, 616) named the gas ozone and noticed its powerful oxidizing properties. It is said to be an ever-present constituent of the air, giving to the sky its blue color; present much more in the country and near the seashore than in the air of cities (Hartley, *J. C.*, 1881, **39**, 57 and 111; Houzeau, *C. r.*, 1872, **74**, 712). Ozone is always mixed with ordinary oxygen, partly due to dissociation of the ozone molecule, which is stable only at low temperatures (Hautefeuille and Chappuis, *C. r.*, 1880, **91**, 522 and 815). It is prepared by the action of the electric discharge upon oxygen (Bichat and Guntz, *C. r.*, 1888, **107**, 344; Wills, *B.*, 1873, **6**, 769). By the oxidation of moist phosphorus at ordinary temperature (Leeds, *A.*, 1879, **198**, 30; Marignac, *C. r.*, 1845, **20**, 808). By electrolysis of dilute sulphuric acid, using lead electrodes Planti, *C. r.*, 1866, **63**, 181). By the action of concentrated sulphuric acid on potassium permanganate (Schoenbein, *J. pr.*, 1862, **86**, 70 and 377). Many readily oxidized organic substances form some ozone in the process of oxidation (Belluci, *B.*, 1879, **12**, 1699). Ozone is a gas, the blue color of which can be plainly noticed in tubes one metre long. Its odor reminds one somewhat of chlorine and nitrogen peroxide, noticeable in one part in 1,000,000. In strong concentrations it acts upon the respiratory organs, making breathing difficult. When somewhat concentrated it attacks the mucous membrane. It caused death to small animals which have been made to breathe it. For further concerning the physiological action, see Binz, *C. C.*, 1873, 72. Its *specific gravity*

is 1.658 (Soret, *A.*, 1866, **138**, 4). It has been liquefied to a deep-blue liquid, *boiling at* − 106° (Olszewski, *M.*, 1887, **8**, 230). The gas is sparingly soluble in water (Carius, *B.*, 1873, **6**, 806). It decomposes somewhat into inactive oxygen at ordinary temperature, and completely when heated above 300°, with increase of volume. A number of substances decompose ozone, without themselves being changed; *e. g.*, platinum black, platinum sponge, oxides of gold, silver, iron and copper, peroxides of lead, and manganese, potassium hydroxide, etc. It is one of the most active oxidizing agents known, the presence of water being necessary. When ozone acts as an oxidizing agent, there is no change in volume; but one-third of the oxygen entering into the reaction, inactive oxygen remaining.

Moist ozone oxidizes all metals except gold and platinum to the highest possible oxides.

Pb″ becomes PbO_2
Sn″ becomes SnO_2
Hg′ becomes **Hg″**
Bi‴ becomes Bi_2O_5
Pd″ becomes PdO_2
Cr‴ becomes Cr^{VI}
Fe″ becomes Fe_2O_3; in presencé of **KOH**, K_2FeO_4
Mn″ becomes MnO_2; in presence of H_2SO_4 or HNO_3, $HMnO_4$ is formed.
Co″ becomes **Co‴**
Ni″ becomes **Ni‴**. With the salts of nickel and cobalt the action is slow, rapid with the moist hydroxides.
$K_4Fe(CN)_6$ becomes $K_3Fe(CN)_6$
N_2O_3 becomes HNO_3, in absence of water NO_2 is formed
SO_2 becomes H_2SO_4
H_2S becomes **S** and H_2O, the sulphur is then oxidized to H_2SO_4 (Pollacci, *C. C.*, 1884, 484)
P and PH_3 become H_3PO_4
HCl becomes **Cl** and H_2O
HBr becomes **Br** and H_2O
I becomes HIO_3 and HIO_4 (Ogier, *C. r.*, 1878, **86**, 722)
HI and **KI** become **I** and H_2O, then I^V

Most organic substances are decomposed: indigo is bleached much more rapidly than by chlorine (Houzeau, *C. r.*, 1872, **75**, 349).

Alcohol and ether are rapidly oxidized to aldehyde and acetic acid.

Ozone is usually detected by the liberation of iodine from potassium iodide, potassium iodide starch paper being used. Because HNO_2 and many other substances give the same reaction, thallium hydroxide paper is preferred by Schoene (*B.*, 1880, **13**, 1508). The paper is colored brown, but the reaction is much less delicate than with potassium iodide starch paper. Chlorine, bromine, iodine and nitrous oxides do not interfere with the following test. Paper is moistened with a 15 per cent solution of potassium iodide to which a 1 per cent alcoholic rosolic acid or phenolphthalein solution has been added until a marked opalescence is produced. A red color is produced by exposure to ozone. The color produced by the rosolic acid is more permanent than the phenolphthalein color. It is estimated quantitatively by passing the gas through a neutral solution of **KI** and titration of the liberated iodine: $O_3 + 2KI + H_2O = O_2 + I_2 + 2KOH$.

Ozone may also be detected by the blue color imparted to guaiacum tincture. Hydrogen peroxide does not produce this effect unless ferrous sulphate solution is added. The most sensitive reagent is a freshly prepared 10 per cent solution of guaiacum gum in 50 per cent water solution of chloralhydrate. (Weber, *Z.*, **43**, 47).

§244. Hydrogen peroxide. $H_2O_2 = 34.016$.

$$H—O—O—H.$$

1. **Properties.**—Pure hydrogen peroxide (99.1 per cent) is a colorless syrupy liquid, boiling at 84° to 85° at 68 mm. pressure. It does not readily moisten the containing vessel. It is volatile in the air, irritating to the skin, and

reacts strongly acid to litmus. The ordinary three per cent solution can be evaporated on the water bath until it contains about 60 per cent H_2O_2, losing about one-half by volatilization. The presence of impurities causes its decomposition with explosive violence. Before final concentration under reduced pressure it should be extracted with ether (Wolffenstein, *B.*, 1894, **27**, 3307). The dilute solutions are valuable in surgery in oxidizing putrid flesh of wounds, etc.; they are quite stable and may be preserved a long time especially if acid (Hanriott, *C. r.*, 1885, **100**, 57). The presence of alkalis decreases the stability. Concentrated solutions evolve oxygen at 20°, and frequently explode when heated to nearly 100°. It contains the most oxygen of any known compound; one-half of the oxygen being available, the other half combining with the hydrogen to form water.

2. **Occurrence.**—In rain water and in snow (Houzeau, *C. r.*, 1870, **70**, 519). It is also said to occur in the juices of certain plants.

3. **Formation.**—(*a*) By the electrolysis of 70 per cent H_2SO_4 (Richarz, *W. A.*, 1887, **31**, 912). (*b*) By the action of ozone upon ether and water (Berthelot, *C. r.*, 1878, **86**, 71). (*c*) By the action of ozone upon dilute ammonium hydroxide (Carius, *B.*, 1874, **7**, 1481). (*d*) By the decomposition of various peroxides with acids. (*e*) By the action of oxygen and water on palladium sponge saturated with hydrogen (Traube, *B.*, 1883, **16**, 1201). (*f*) By the action of moist air on phosphorus partly immersed in water (Kingzett, *J. C.*, 1880, **38**, 3).

4. **Preparation.**—BaO_2 is decomposed by dilute H_2SO_4, the $BaSO_4$ being removed by filtration. The BaO_2 is obtained by heating **BaO** in air or oxygen to low redness. At a higher heat the BaO_2 is decomposed into **BaO** and **O** (Thomsen, *B.*, 1874, **7**, 73). **Sodium peroxide**, Na_2O_2, is formed by heating sodium in air or oxygen (Harcourt, *J. C.*, 1862, **14**, 267); by adding H_2O_2 to **NaOH** solution and precipitating with alcohol. Prepared by the latter method it contains water.

5. **Solubilities.**—It is soluble in water in all proportions; also in alcohol, which solvent it slowly attacks. BaO_2 is insoluble in water, decomposed by acids, including CO_2 and H_2SiF_6 with formation of H_2O_2. Na_2O_2 is soluble in water with generation of much heat. It is a powerful oxidizing agent.

6. **Reactions.** *A.*—**With metals and their compounds.**—Hydrogen peroxide usually acts as a powerful oxidizing agent to the extent of one-half its oxygen. Under certain conditions, however, it acts as a strong reducing agent. Some substances decompose it into H_2O and **O** without changing the substance employed, *e. g.*, gold, silver, platinum, manganese dioxide, charcoal, etc. (Kwasnik, *B.*, 1892, **25**, 67). Many metals are oxidized to the highest oxides, *e. g.*, **Al**, **Fe**, **Mg**, **Tl**, **As**, etc. Gold and platinum are not attacked.

1. Pb'' becomes PbO_2 (Schoenbein, *J. pr.*, 1862, **86**, 129; Jannasch and Lesinsky, *B.*, 1893, **26**, 2334).

2. Ag_2O becomes **Ag** and **O**.

3. **HgO** becomes **Hg** and **O**.

4. Au_2O_3 becomes **Au** and **O**.

5. As''' becomes As^V.

6. Sn'' becomes Sn^{IV}.

7. Bi''' becomes Bi^V.

8. Cu'' in alkaline solution (Fehling's solution) becomes Cu_2O (Hanriott, *Bl.*, 1886, (2), **46**, 468).

9. Fe'' becomes Fe''' (Traube, *B.*, 1884, **17**, 1062).

10. Tl' becomes Tl_2O_3 (Schoene, *A.*, 1879, **196**, 98).

11. Cr''' becomes Cr^{VI} in alkaline mixture (Lenssen, *J. pr.*, 1860, **81**, 278).

12. Cr^{VI} with H_2SO_4 gives a blue color, $HCrO_4$, *perchromic acid*, soon changing to green by reduction to Cr'''. By passing the air or vapor through a chromic acid solution, ozone is separated from hydrogen peroxide, the latter being decomposed (Engler and Wild, *B.*, 1896, **29**, 1940).

13. Mn'' in alkaline mixture becomes MnO_2. In presence of **KCN** a separation from **Zn** (Jannasch and Niederhofheim, *B.*, 1891, **24**, 3945; Jannasch, *Z. anorg.*, 1896, **12**, 124 and 134).

Mn''^{+n} with H_2SO_4 forms $MnSO_4$, oxygen being evolved both from the H_2O_2 and from the **Mn** compound (Brodie, *J. C.*, 1855, **7**, 304; Lunge, *Z. angew.*, 1890, 6).

14. BaO, SrO, and CaO become the peroxides.

15. $NaOH$ becomes $Na_2O_2.8H_2O$.

16. NH_4OH becomes NH_4NO_2 (Weith and Webber, *B.*, 1874, **7**, 17 and 45).

17. Ti^{IV} is oxidized to pertitanic acid, H_2TiO_4, with the production of a yellow color which constitutes a very delicate test for H_2O_2.

B.—**With non-metals and their compounds.**

1. $K_4Fe(CN)_6$ becomes $K_3Fe(CN)_6$ (Weltzien, *A.*, 1866, **138**, 129): in alkaline solution the reverse action takes place: $2K_3Fe(CN)_6 + 2KOH + H_2O_2 = 2K_4Fe(CN)_6 + 2H_2O + O_2$ (Baumann, *Z. angew.*, 1892, 113).

2. O_3 becomes O_2 (Schoene, *l. c.*, page 239).

3. H_3PO_2 becomes H_3PO_4.

4. H_2S and sulphides, and SO_2 and sulphites, become H_2SO_4 or sulphates (Classen and Bauer, *B.*, 1883, **16**, 1061).

5. **Cl** becomes **HCl** (Schoene, *l. c.*, page 254). It is a valuable reagent for the estimation of chloride of lime: $CaOCl_2 + H_2O_2 = CaCl_2 + H_2O + O_2$ (Lunge, *Z. angew.*, 1890, 6).

6. **I** becomes **HI** (Baumann, *Z. angew.*, 1891, 203 and 328). **KCl**, **KBr**, and **KI** liberate oxygen from H_2O_2 but no halogen is set free; except that with commercial H_2O_2 free iodine may always be obtained from **KI** (Schoene, *A.*, 1879, **195**, 228; Kingzett, *J. C.*, 1880, **37**, 805).

7. **Ingition.**—The peroxide of barium is formed by igniting BaO to dull redness; strong ignition causes decomposition of the BaO_2 into BaO and O. The peroxide of calcium cannot be formed by ignition of lime in air or oxygen.

8. **Detection.**—In a dilute solution of tincture of guaiac mixed with malt infusion or ferrous sulphate, a blue color is obtained when H_2O_2 is added. To the solution supposed to contain H_2O_2 add a few drops of lead acetate; then **KI**, starch, and a little acetic acid; with H_2O_2 a blue color is produced (Schoenbein, *l. c.*; Struve, *Z.*, 1869, 8, 274). As confirmatory, its action on $KMnO_4$ and on $K_2Cr_2O_7$ should be observed. A ten per cent solution of ammonium molybdate with equal parts of concentrated sulphuric acid gives a characteristic deep yellow color with H_2O_2 (Deniges, *C. r.*, 1890, **110**, 1007; Crismer, *Bl.*, 1891, (3), **6**, 22). H_2O_2 gives some extremely delicate color tests with the analine bases (Ilosvay, *B.*, 1895, **28**, 2029; Deniges, *J. Pharm.*, 1892, (5), **25**, 591; Weber, *Z.*, **43**, 47). Titanium sulphate, $Ti(SO_4)_2$, in acid solution gives an extremely delicate test for H_2O_2, a yellow color being produced. On the addition of caustic alkali a yellowish orange precipitate is produced which redissolves in excess of the reagent.

9. **Estimation.**—(*a*) By measuring the amount of oxygen liberated with **MnO** (Hanriott, *Bl.*, 1885, (2), **43**, 468). (*b*) By the amount of standard $KMnO_4$ reduced, or by measuring the volume of oxygen set free: $2KMnO_4 + 3H_2SO_4 + 5H_2O_2 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$. (*c*) By decomposition of **KI** in presence of an excess of dilute H_2SO_4; and titration of the liberated iodine with standard $Na_2S_2O_3$. (*d*) Dissolve a weighed sample of BaO_2 in dilute **HCl**, add $K_3Fe(CN)_6$; transfer to an azotometer and add **KOH**. The volume of oxygen is a measure of the amount of H_2O_2 (Baumann, *l. c.*).

§245. Fluorine. F = 19.00. Valence one.

Since Davy's experiments in 1813, many others have attempted the isolation of fluorine. In his zeal the unfortunate Louyet fell a victim to the poisonous fumes which he inhaled. Faraday, Gore, Fremy, and others took up the problem in succession, but it was not ultimately solved until H. Moissan, in 1886, produced a gas which the chemical section of the French Academy of Sciences decided to be fluorine. Many ingenious experiments had been made in order to obtain fluorine in a separate state, but it was found that it invariably combined with some portion of the material of the vessel in which the operation was conducted. The most successful of the early attempts to isolate fluorine appears to have been made, at the suggestion of Davy, in a vessel of fluor-spar itself, which could not, of course, be supposed to be in any way affected by it. Moissan's method was as follows: The hydrofluoric acid having been very carefully obtained pure, a little potassium hydrofluoride was dissolved in it to improve its conducting power, and it was subjected to the action of the electric current in a U tube of platinum, down the limbs of which the electrodes were inserted; the negative electrode was a rod of platinum, and the positive was made of an alloy of platinum with 10 per cent of iridium. The U tube was provided with stoppers of fluor-spar, and platinum delivery tubes for the gases, and was cooled to —23°. The gaseous fluorine, which was extricated at the positive electrode, was colorless, and possessed the properties of chlorine, but much more strongly marked. It decomposed water immediately, seizing upon its hydrogen, and liberating oxygen in the ozonized condition; it exploded with hydrogen, even in the dark, and combined, with combustion, with most metals and non-metals, even with boron and silicon in their crystallized modifications. **As**, **Sb**, **S**, **I**, alcohol, ether, benzol and petroleum took fire in the gas. Carbon was not attacked by it (Moissan, 1886, *C. r.*, **103**, 202 and 256; *J. C.*, **50**, 1886, 849 and 976; *A. Ch.*, 1891, (6), **24**, 224).

1. **Properties.**—A gas of light greenish-yellow color and strong pungent odor; *Specific gravity*, 1.313 (Moissan, *C. R.*, 109). When cooled to a temperature of about − 187° it condenses to a mobile yellow liquid. Specific gravity of this liquid is 1.14. At − 223° C., fluorine solidifies to a pale yellow solid. The solid loses its yellow color and becomes perfectly white at − 252° (Moissan and Dewar, *C. R.*, 1903, 136).

2. **Occurrence.**—Fluorine does not occur free in nature, but is found in considerable quantities in combination with calcium in the mineral fluorspar, CaF_2. Its other fairly common compounds are cryolite, Na_3AlF_6 and apatite, $Ca_5(PO_4)_3F$.

Fluorine, in several characteristics, appears as the first member of the Chlorine Series of Elements. It cannot be preserved in the elemental state, as it combines with the materials of vessels (except fluor-spar), and instantly decomposes water, forming *hydrofluoric acid*, **HF**, an acid prepared by acting on calcium fluoride with sulphuric acid (*a*). Fluorine also combines with silicon, forming SiF_4, *silicon fluoride*, a gaseous compound, generally prepared by the action of concentrated sulphuric acid on calcium fluoride and silicic anhydride. (*b*). On passing silicon fluoride into water, a part of it is transposed by the water, forming silicic and hydrofluoric acids (*c*); but this hydrofluoric acid does not remain free, but combines with the other part of the fluoride of silicon, as fluosilicic acid (*hydrofluosilicic acid*), $(HF)_2SiF_4$ or H_2SiF_6 (*d*) (Offermann, *Z. angew.*, 1890, 617). This acid is used as a reagent; forming metallic fluosilicates (silicofluorides), soluble and insoluble (§246).

a. $CaF_2 + H_2SO_4 = CaSO_4 + 2HF$

b. $2CaF_2 + SiO_2 + 2H_2SO_4 = 2CaSO_4 + 2H_2O + SiF_4$

c. $SiF_4 + 4H_2O = Si(OH)_4 + 4HF$ (not remaining free)

d. $2HF + SiF_4 = H_2SiF_6$

c and d. $3SiF_4 + 4H_2O = Si(OH)_4 + 2H_2SiF_6$

§246. Hydrofluoric acid. $HF = 20.008$.

$H'F^{-\prime}$, $H-F$.

A colorless, intensely corrosive gas, soluble in water to a liquid that reddens litmus, rapidly corrodes glass, porcelain, and the metals, except platinum and gold (lead but slightly). Both the solution and its vapor act on the flesh as an insidious and virulent caustic, giving little warning, and causing obstinate ulcers. The anhydrous acid at 25° has a vapor density of 20, indicating that the molecule at this temperature is H_2F_2. But at 100° it is only 10, indicating that at that temperature the molecule is HF. The anhydrous liquid acid boils at 19.44° and does not solidify at —34.5°.

The **fluorides** of the alkali metals are freely **soluble in water**, the solutions alkaline to litmus and slightly corrosive to glass: the fluorides of the alkaline earth metals are insoluble in water; of copper, lead, zinc and ferricum, sparingly soluble; of silver and mercury readily soluble. Fluorides are **identified** by the action of the acid upon glass.

Calcium chloride solution forms, in solution of fluorides or of hydrofluoric acid, a gelatinous and transparent precipitate of *calcium fluoride*, CaF_2, slightly soluble in cold hydrochloric or nitric acid and in ammonium chloride solution. **Barium chloride** precipitates, from free hydrofluoric acid less perfectly than from fluorides, the voluminous, white, *barium fluoride*, BaF_2. Silver nitrate gives no precipitate.

Sulphuric acid transposes fluorides, forming *hydrofluoric acid*, HF (§245, *a*). The gas is distinguished from other substances by *etching hard glass* previously prepared by coating imperviously with (melted) wax, and writing through the coat. The operation may be conducted in a small leaden tray, or cup formed of sheet lead; the pulverized fluoride being mixed with sulphuric acid to the consistence of paste.

If the fluoride be mixed with **silicic acid**, we have, instead of hydrofluoric acid, *silicon fluoride*, SiF_4 (§245, *b*): a gas which does not attack glass, but when passed into water produces fluosilicic acid, H_2SiF_6 (§245, *c* and *d*). See below.

Also, heated with acid sulphate of potassium, in the dry way, fluorides disengage hydrofluoric acid. If this operation be performed in a small test-tube, the surface of the glass above the material is corroded and roughened: $CaF_2 + 2KHSO_4 = CaSO_4 + K_2SO_4 + 2HF$. By heating a mixture of borax, acid sulphate of potassium, and a fluoride, fused to a bead on the loop of platinum wire, in the clear flame of the Bunsen gas-lamp, an evanescent *yellowish-green color* is imparted to the flame.

§247. Fluosilicic acid. $H_2SiF_6 = 144.316$.

Fluosilicic acid * (*hydrofluosilicic acid*), $(HF)_2SiF_4$, or H_2SiF_6, is soluble in water and forms metallic fluosilicates (*silicofluorides*), mostly soluble in water; those of barium (§186, 6*i*), sodium and potassium, being only slightly soluble in water, and made quite insoluble by addition of alcohol.

* *Fluosilicic acid* is directed to be prepared by taking one part each of fine sand and finely powdered fluor-spar, with six to eight parts of concentrated sulphuric acid, in a small stoneware bottle or a glass flask, provided with a wide delivery-tube, dipping into a little mercury in a small porcelain capsule, which is set in a large beaker containing six or eight parts of water. The stoneware bottle or flask is set in a small sand-bath, with the sand piled about it, as high as the material, and gently heated from a lamp. Each bubble of gas decomposes with deposition of gelatinous silicic acid. When the water is filled with this deposit, it may be separated by straining through cloth and again treating with the gas for greater concentration. The strained liquid is finally filtered and preserved for use.

Potassium fluosilicate is precipitated translucent and gelatinous. Ammonium hydroxide precipitates silicic acid with formation of ammonium fluoride. With concentrated sulphuric acid, they disengage hydrofluoric acid, **HF**. By heat, they are resolved into fluorides and silicon fluoride: $BaSiF_6 = BaF_2 + SiF_4$.

§248. Silicon. Si = 28.3. Valence four (§15).

There are three modifications of silicon: (*a*) *Amorphous.*—A dark brown powder; *specific gravity*, 2.0; non-volatile; infusible; burns in the air, forming SiO_2, and in chlorine, forming $SiCl_4$. It is not attacked by acids except **HF**: $Si + 6HF = H_2SiF_6 + 2H_2$. It is dissolved by **KOH** with evolution of hydrogen. (*b*) *Graphitoidal.*—May be fused, but is not oxidized upon ignition in air or in oxygen. It is not attacked by **HF**, but is dissolved by a mixture of **HF** and HNO_3, forming H_2SiF_6. It is attacked slowly by fused **KOH**. (*c*) *Adamantine silicon*, crystalline silicon.—Grayish-black, lustrous, octahedral crystals, formed by fusing the graphitoidal form. *Specific gravity*, 2.49 at 10° (Woehler, *A.*, 1856, **97**, 261). It scratches glass but not topaz. It melts between the melting points of pig iron and steel, 1100° to 1300°. In chemical properties it is very similar to the graphitoidal form, being attacked with even greater difficulty. Silicon is never found free in nature, but always in combination as silica, SiO_2, or as silicates.

Amorphous silicon is formed by passing vapor of $SiCl_4$ over heated potassium; by heating magnesium in SiF_4 vapor; by heating a mixture of **Mg** and SiO_2; by electrolysis of a fused silicate. It is readily prepared by heating a mixture of magnesium, one part, with sand, four parts, in a wide test-tube of hard glass (Gattermann, *B.*, 1889, **22**, 186). The graphitoidal form is crystalline and by many is said to be the same as the adamantine form. Method of preparation essentially the same (Warren, *C. N.*, 1891, **63**, 46). The crystalline form is made by fusing a silicate or K_2SiF_6 with **Al**; by passing vapors of $SiCl_4$ over heated **Na** or **Al** in a carbon crucible (Deville, *A. Ch.*, 1857, (3), **49**, 62; Deville and Caron, *A. Ch.*, 1863, (3), **67**, 435; Woehler, *l. c.*).

§249. Silicon dioxide. $SiO_2 = 60.3$.

(Silicic anhydride; silica.)

Silicic acid. $H_2SiO_3 = 78.316$.

$Si^{IV}O^{-2}_2$ and $H'_2Si^{IV}O^{-''}_3$, $O = Si = O$ and $H - O - \overset{O}{\overset{\|}{Si}} - O - H$.

1. **Properties.**—**Silica**, *silicic anhydride*, SiO_2, is a white, stable, infusible solid; insoluble in water or acids; soluble in fixed alkalis with formation of silicates. *Specific gravity* of quartz, 2.647 to 2.652; of amorphous silica, 2.20 at 15.6°.

Silicic acid, *silicon hydroxide*, H_2SiO_3, is a white, gelatinous solid, generally insoluble in water, and soluble in mineral acids. A dilute solution in water is obtained by dialysis of the fixed alkali silicate with an excess of **HCl** until the chlorides are all removed. It may be boiled for some time before the acid precipitates out. Upon standing silicic acid soon separates.

2. **Occurrence.**—Silicon is never found free in nature; it is always combined with oxygen in the form of silicon dioxide, SiO_2, as quartz, opal, flint, sand, etc.; or the silicon dioxide is in combination with bases as silicates; asbestos, soapstone, mica, cement, glass, etc. All geological formations except chalk contain silicon as the dioxide or as a silicate.

3. **Formation.**—Crystalline silica is formed by passing silicon fluoride into water, forming silicic acid and fluosilicic acid: $3SiF_4 + 3H_2O = H_2SiO_3 + 2H_2SiF_6$. The precipitate of silicic acid is dissolved in boiling **NaOH** and then heated in sealed tubes. Below 180° crystals of tridymite are formed, and above 180° crystals of quartz (Maschke, *Pogg.*, 1872, **145**, 549).

4. **Preparation.**—Pure amorphous silica is prepared by fusing finely powdered quartz with six parts of sodium carbonate, dissolving the cooled mass in water, and pouring into fairly concentrated hydrochloric acid. The precipitate is filtered, well washed and ignited. Or SiF_4 vapors are passed into water (**§246**) and the gelatinous precipitate washed, dried and ignited. Crystalline

silica is prepared by fusing silicates with microcosmic salt or with borax (Rose, *J. pr.*, 1867, **101**, 228).

Silicic acid.—The various hydroxides of silica act as weak acids. Metasilicic acid, H_2SiO_3, has been isolated; it is formed by decomposing silicon ethoxide, $Si(OC_2H_5)_4$, with moist air (Ebelmen, *J. pr.*, 1846, **37**, 359). Also by dialysis of a mixture of sodium silicate with an excess of hydrochloric acid until the chlorides are all removed, concentrating, allowing to gelatinize, and drying over sulphuric acid. Other hydroxides, acids, have been isolated, but there is some question as to their exact composition.

5. **Solubilities.**—**Silica,** SiO_2, is insoluble in water or acids except **HF**, which dissolves it with formation of gaseous silicon fluoride, SiF_4 (§246). Of the *silicates* only those of the fixed alkalis are soluble in water, water glass. These silicates in solution are readily decomposed by acids, including carbonic acid, forming silicic acid, gelatinous. While anhydrous silicic anhydride, SiO_2, is insoluble in mineral acids, the freshly precipitated hydroxide, silicic acid, is soluble in those acids. Silicic acid is decomposed by evaporation to dryness in presence of mineral acids, with separation of the anhydrous SiO_2; which is insoluble in more of the same acids, which previously had effected its solution.

The most of the silicates found in nature are of complex composition. They are combinations of SiO_2 with bases. They are, as a rule, insoluble in water or acids.

6. **Reactions.**—Solutions of the alkali silicates precipitate solutions of all other metallic salts with formation of insoluble silicates; they are decomposed by acids with separation of silicic acid, a gelatinous precipitate, soluble in hydrochloric acid. Evaporation decomposes silicic acid with separation of insoluble silicic anhydride, SiO_2. Ammonium salts precipitate gelatinous silicic acid from solutions of potassium or sodium silicate. Therefore in the process of analysis the silicic acid, not removed in the first group by hydrochloric acid, will be precipitated in the third group on the addition of ammonium chloride.

Silica, SiO_2, is soluble in hot fixed alkalis forming silicates; it is not soluble in ammonium hydroxide, nor are solutions of alkali silicates precipitated on addition of ammonium hydroxide as they are on the addition of ammonium salts. Boiling SiO_2 with the fixed alkali carbonates forms soluble silicates with greater or less readiness. Nearly all silicates are decomposed by heating in sealed tubes to 200° with concentrated **HCl** or H_2SO_4.

7. **Ignition.**—Silicates fused with the alkalis form soluble alkali silicates, and oxides of the metal previously in combination. If alkali carbonates are employed the same products are formed with evolution of CO_2. Preferably a mixture (in molecular proportions) of potassium and sodium carbonates, four parts, should be used to one part of the insoluble silicate. Silica, SiO_2, is also changed to a soluble silicate by fusing with fixed alkali hydroxides or carbonates.

SiO_2 does not react with K_2SO_4 or Na_2SO_4, even when fused at a very high temperature (Mills and Meanwell, *J. C.*, 1881, **39**, 533). In the fused bead of microcosmic salt particles of silica swim *undissolved*. If a silicate be taken, its base will, in most cases, be dissolved out, leaving a "*skeleton of silica*" undissolved in the liquid bead. But with a bead of sodium carbonate, silica (and most silicates) fuse to a clear *glass* of silicate.

Silica is separated from the fixed alkalis in natural silicates, by mixing the latter in fine powder with three parts of precipitated calcium carbonate, and one-half part of ammonium chloride, and heating in a platinum crucible to redness for half an hour, avoiding too high a heat. On digesting in hot water, the solution contains all the alkali metals, as chlorides, with calcium chloride and hydroxide.

8. **Detection.**—*Silicates* are detected by conversion into the anhydride, SiO_2. The silicate is fused with about four parts of a mixture of potassium and sodium carbonates, digested with warm water, filtered, and evaporated to dryness with an excess of hydrochloric acid. The dry residue is moistened with concentrated **HCl** and thoroughly pulverized; water is added and the precipitate of SiO_2 is thoroughly washed. Further confirmation may be obtained by warming the precipitate of SiO_2 with calcium fluoride and sulphuric acid (in lead or platinum dishes), forming the gaseous silicon fluoride, SiF_4. This is passed into water where it is decomposed into gelatinous silicic acid and fluosilicic acid: $3SiF_4 + 3H_2O = H_2SiO_3 + 2H_2SiF_6$ (§**246**). *Silica*, SiO_2, is usually treated as directed for silicates, but may be at once warmed with calcium fluoride and sulphuric acid.

9. **Estimation.**—The compound containing a silicate or silica is fused with fixed alkali carbonates as directed under detection, and the amount of well-washed SiO_2 determined by weighing after ignition.

§250. Phosphorus. P = 31.04. Usual valence three or five (§11).

1. **Properties.**—Phosphorus is prepared in several allotropic modifications. *Specific gravity* of the yellow, solid, at 20°, 1.82321; liquid, at 40°, 1.74924; solid, at 44.2° 1.814 (Damien, 1881). At ordinary temperatures it is brittle and easily pulverized. At 44.1° (Burgess, *Wash. Acad. of Sci.*, 1–18) it melts, but may be cooled in some instances (under an alkaline liquid) as low as +4° without solidifying. When it solidifies from these lower temperatures, as it does by stirring with a solid substance, the temperature immediately rises to about 45°. *Boiling point*, 287.3° at 762 mm. pressure (Schroetter, *A.*, 1848, **68**, 247; Kopp, *A.*, 1855, **94**, 129). The density of the vapor at 1040° is 4.50 (Deville and Troost, *C. r.*, 1863, **56**, 891). The computed density for the molecule P_4 is 4.294. At a white heat the density, 3.632, indicates dissociation of the molecule to P_2 (Meyer and Biltz, *B.*, 1889, **22**, 725). *Specific gravity* of the red amorphous modification at 0°, 2.18 (Jolibois, *C. r.*, 149, 287–289).

Ordinary crystalline yellow stick phosphorus is a nearly colorless, transparent solid; when cooled slowly it is nearly as clear as water. In water containing air it becomes coated with a thin whitish film. If melted in fairly large quantities and cooled slowly it forms dodecahedral and octahedral crystals (Whewell, *C. N.*, 1879, **39**, 144). Heated in absence of air above the boiling point it sublimes as a colorless gas, depositing lustrous transparent crystals (Blondlot, *C. r.*, 1866, **63**, 397). At low temperatures phosphorus oxidizes slowly in the air with a characteristic odor, probably due to the formation of ozone and phosphorous oxide, P_2O_3 (Thorpe and Tutton, *J. C.*, 1890, **57**, 573). It ignites spontaneously in the air at 44.5°, burning with a bright yellowish white light producing much heat. From the finely divided state, as from the evaporation

of its solution in carbon disulphide, it ignites spontaneously at temperatures at which the compact phosphorus may be kept for days. It must be preserved under water. Great precaution should be taken in working with the ordinary or yellow phosphorus. Burns caused by it are very painful and heal with great difficulty. Ordinary phosphorus is luminous in the dark, but it has been shown that the presence of at least small amounts of oxygen are necessary. The presence of H_2S, SO_2, CS_2, Br, Cl, etc., prevent the glowing (Schroetter, *J. pr.*, 1853, **58**, 158; Thorpe, *Nature*, 1890, **41**, 523). Upon heating in absence of air, better in sealed tubes, to 300° it is changed to the red modification (Meyer, *B.*, 1882, **15**, 297).

Red phosphorus is a dull carmine-red tasteless powder. It is not poisonous, while the ordinary yellow variety is intensely poisonous, 200 to 500 milligrams being sufficient to cause death. While the yellow modification is so readily and dangerously combustible when exposed to the air even at ordinary temperatures, the red variety needs no special precautions for its preservation. It does not melt when heated to redness in sealed tubes, but is partially changed to the yellow crystalline form (Hittorf, *Pogg.*, 1865, **126**, 193). If amorphous phosphorus be distilled in the absence of air, it is changed to the crystalline form, action beginning at 260°. If ordinary red phosphorus is heated to 400° for sixty hours, in absence of air, it becomes red pyromorphic phosphorus whose density is 2.37. Heated to 725° this phosphorus melts, and if suddenly cooled becomes a violet-colored mass (Jolibois, *C. r.*, **149**, 287–289). Heated in the air from 250° to 260° it takes fire (Schroetter, *l. c.*). A black crystalline metallic variety of phosphorus is described by Hittorf (*l. c.*); also Remsen and Kaiser (*Am.*, 1882, **4**, 459) describe a light plastic modification. Phosphorus is largely used in match-making. Yellow phosphorus is used in the ordinary match, and the red (amorphous) in the safety matches, the phosphorus being on a separate surface.

2. **Occurrence.**—It is never found free in nature. It is found in the primitive rocks as calcium phosphate, occasionally as aluminum, iron, or lead phosphate, etc. Plants extract it from the soil, and animals from the plants. Hence traces of it are found in nearly all animal and vegetable tissues; more abundantly in the seeds of plants and in the bones of animals.

3. **Formation.**—Ordinary phosphorus is formed by heating calcium or lead phosphates with charcoal. The yield is increased by mixing the charcoal with sand or by passing HCl gas over the heated mixture. By igniting an alkali or alkaline earth phosphate with aluminum (Rossel and Frank, *B.*, 1894, **27**, 52). Red phosphorus is formed by the action of light, heat or electricity on ordinary phosphorus (Meyer, *B.*, 1882, **15**, 297). By heating ordinary phosphorus with a small amount of iodine (Brodie, *J. pr.*, 1853, **58**, 171).

4. **Preparation.**—Ordinary phosphorus is prepared from bones. They are first burned, which leaves a residue, consisting chiefly of $Ca_3(PO_4)_2$; then H_2SO_4 is added, producing soluble calcium tetrahydrogen diphosphate (*a*). After filtering from the insoluble calcium sulphate the solution is evaporated and ignited, leaving calcium metaphosphate (*b*). Then fused with charcoal, reducing two-thirds of the phosphorus to the free state (*c*). The mixture of sand, SiO_2, with the charcoal is preferred, in which case the whole of the phosphorus is reduced (*d*). Hydrochloric acid passed over red-hot calcium phosphate and charcoal reduces the whole of the phosphorus. This process works well in the laboratory, and has also been successfully employed on a larger scale. Either of the calcium phosphates may be used (*e*) and (*f*).

(*a*) $Ca_3(PO_4)_2 + 2H_2SO_4 = 2CaSO_4 + CaH_4(PO_4)_2$

(*b*) $CaH_4(PO_4)_2 + \text{ignition} = Ca(PO_3)_2 + 2H_2O$

(*c*) $3Ca(PO_3)_2 + 10C = Ca_3(PO_4)_2 + 10CO + P_4$

(*d*) $2Ca(PO_3)_2 + 10C + 2SiO_2 = 2CaSiO_3 + P_4 + 10CO$

(*e*) $2Ca_3(PO_4)_2 + 16C + 12HCl = 6CaCl_2 + P_4 + 16CO + 6H_2$

(*f*) $2Ca(PO_3)_2 + 12C + 4HCl = 2CaCl_2 + P_4 + 12CO + 2H_2$

Red or amorphous phosphorus is prepared by heating ordinary phosphorus for a long time (40 hours) at 240° to 250° in absence of air. At 260° the reverse change takes place. If the heating is under pressure and at 300°, the change to the red phosphorus is almost immediate. It is washed with CS_2 to remove all traces of yellow phosphorus and is dried at 100°.

5. **Solubilities.**—A trace of phosphorus dissolves in water. Alcohol dissolves 0.4, ether 0.9, olive oil 1.0, and turpentine 2.5 per cent of it, while carbon disulphide dissolves 10 to 15 times its own weight. Red phosphorus is insoluble in water, ether, or carbon disulphide.

6. **Reactions.**—When phosphorus is boiled with a fixed alkali or alkaline earth hydroxide, phosphorus hydride, phosphine (§249), PH_3, and a hypophosphite (§250) are formed. Phosphorus, when warmed in an atmosphere of **N** or CO_2, combines directly with many metals to form phosphides. These phosphides are usually brittle solids decomposing with water or dilute acids with formation of phosphoretted hydrogen, PH_3. In nearly all the reactions of phosphorus both varieties react the same, the red variety with much less intensity, and frequently requiring the aid of heat. It is ignited when brought in contact with PbO_2, Pb_3O_4, HgO, Ag_2O, CrO_3, $K_2Cr_2O_7$ and when heated with CuO or MnO_2. Solutions of platinum, gold, silver, and copper salts are decomposed by phosphorus with separation of the corresponding metal (Boettger, *J. C.*, 1874, **27**, 1060).

With HNO_3, H_3PO_4 and **NO** are formed; when heated with KNO_3 a rapid oxidation takes place.

It combines with oxygen, forming P_2O_3 or P_2O_5. With yellow phosphorus the reaction begins at ordinary temperature; with the red variety not till heated to 250° to 260° (Baker, *J. C.*, 1885, **47**, 349).

Water is decomposed at 250°, forming PH_3 and H_3PO_4 (Schroetter, *l. c.*).

Combination with red phosphorus and sulphur takes place at ordinary temperatures, forming P_2S_3 or P_2S_5, depending upon the proportion of each employed (Kekulé, *A.*, 1854, **90**, 310). With ordinary phosphorus the action is explosive. Sulphides of phosphorus with formulas P_4S_3 and P_4S_7 have also been prepared. (Stock, *B.*, **43**, 414, 1223.)

Cl or **Br** react with incandescence at ordinary temperatures, forming trihalogen or pentahalogen compounds, depending upon the amount of halogen employed. With iodine, PI_3 is formed.

The halogen compounds of phosphorus are decomposed by water with formation of the corresponding hydracids and phosphorous or phosphoric acids, depending upon the degree of oxidation of the phosphorus. In the presence of water phosphorus is oxidized to H_3PO_4 by **Cl**, **Br**, **I**, $HClO_3$, $HBrO_3$, or HIO_3 with formation of the corresponding hydracid:

$$P_4 + 10Cl_2 + 16H_2O = 4H_3PO_4 + 20HCl.$$

7. **Ignition.**—When sodium carbonate is heated to redness with phosphorus, the carbonic anhydride is reduced and carbon is set free. Phosphorus heated with magnesium in a vapor of carbon dioxide forms P_2Mg_3, which can be heated to redness in absence of air without decomposition. Heated in the air it becomes oxidized (Blunt, *A. Ch.*, 1865, (4), **5**, 487). Phosphorus also combines with **Cu**, **Ag**, **Cd**, **Zn** and **Sn** when it is heated with these elements in sealed tubes. It does not combine with **Al** and but slightly with **Fe** (Emmerling, *J. C.*, 1879, **36**, 508).

8. **Detection.**—By its phosphorescence; by formation of PH_3 when boiled with **KOH** (Hofmann, *B.*, 1871, **4**, 200); by oxidation to H_3PO_4 and detection as such (§**75**, *6d*).

9. **Estimation.**—Oxidation to H_3PO_4, precipitation with magnesia mixture as $MgNH_4PO_4$, ignition to, and weighing as $Mg_2P_2O_7$ (§**189**, *9*).

§251. Phosphine. $PH_3 = 34.064$.

$$P^{-'''}H'_3, \quad H-P(-H)-H$$

Phosphine, PH_3, is a colorless gas having a very disagreeable odor. As usually prepared, it is spontaneously inflammable, burning in the air with formation of metaphosphoric acid: $2PH_3 + 4O_2 = 2HPO_3 + 2H_2O$. It is liquified and frozen at very low temperatures; *boiling point*, about —85°; *melting point*, —132.5° (Olszewski, *M.*, 1886, **7**, 371). It is very poisonous, sparingly soluble in water, which solution has the peculiar odor of the gas and has an exceedingly bitter taste. It is formed by boiling phosphorus with a fixed alkali or alkaline earth hydroxide (*a*); by ignition of H_3PO_2 or H_3PO_3 (*b*); by ignition of hypophosphites (*c*); by the decomposition of the alkaline earth phosphides with water or dilute acids (*d*):

(*a*) $P_4 + 3KOH + 3H_2O = 3KH_2PO_2 + PH_3$

(*b*) $2H_3PO_2 = HPO_3 + PH_3 + H_2O$

$4H_3PO_3 = 3HPO_3 + PH_3 + 3H_2O$

(*c*) $4NaH_2PO_2 = Na_4P_2O_7 + 2PH_3 + H_2O$

(*d*) $Ca_3P_2 + 6H_2O = 3Ca(OH)_2 + 2PH_3$

$Ca_3P_2 + 6HCl = 3CaCl_2 + 2PH_3$

It is a strong reducing agent; transposes many metallic solutions: $3CuSO_4 + 2PH_3 = Cu_3P_2 + 3H_2SO_4$; reduces solutions of silver and gold to the metallic state: $8AgNO_3 + PH_3 + 4H_2O = H_3PO_4 + 8HNO_3 + 8Ag$; is oxidized to H_3PO_4 by hot H_2SO_4, Cl, HClO, HNO_2, HNO_3, H_3AsO_4, etc. A liquid phosphorus hydride, P_2H_4, and a solid, P_4H_2, are known (Besson, *C. r.*, 1890, **111**, 972; Gattermann and Hausknecht, *B.*, 1890, **23**, 1174).

§252. Hypophosphorous acid. $H_3PO_2 = 66.064$.

$$H'_3P'O^{-''}{}_2, \quad H-O-P(-H)=O$$

1. **Properties.**—Hypophosphorous acid was discovered in 1816 by Dulong (*A. Ch.*, 1816, **2**, 141). It is a colorless syrupy liquid; *specific gravity*, 1.493 at 18.8°. At 17.4° it becomes a white crystalline solid (Thomsen, *B.*, 1874, **7**, 994). Although containing three hydrogen atoms it forms but one series of salts, *e. g.*, NaH_2PO_2, $Ba(H_2PO_2)_2$, etc.

2. **Occurrence.**—Not found in nature.

3. **Formation.**—All ordinary metals form hypophosphites except tin, copper and mercurosum. Silver and ferric hypophosphites are very unstable. (1) A

few metals, such as zinc and iron, dissolve in H_3PO_2, giving off hydrogen and forming a hypophosphite. (2) The alkali and alkaline earth salts may be formed by boiling phosphorus with the hydroxides (Mawrow and Muthmann, *Z. angew.*, 1896, ii, 268). (3) As all hypophosphites are soluble, none can be formed by precipitation. All may be formed from their sulphates by transposition with barium hypophosphite. (4) All may be made by adding H_3PO_2 to the carbonates or hydroxides of the metals.

4. **Preparation.**—To prepare pure H_3PO_2, **BaO** and **P** (in small pieces) are warmed in an open dish with water until PH_3 ceases to be evolved. The liquid is filtered and excess of **BaO** is removed by passing in CO_2. After again filtering, the liquid is evaporated to crystallization of the barium salt. This is dissolved in water and decomposed by the calculated quantity of H_2SO_4. The solution is filtered and evaporated in an open dish, care being taken not to heat above 110°. Upon cooling the white crystalline tablets are obtained.

5. **Solubilities.**—The free acid is readily miscible in water in all proportions. The salts are all soluble in water, a number of them are soluble in alcohol.

6. **Reactions.**—*A.*—**With metals and their compounds.** Hypophosphorous acid is a very powerful reducing agent, being oxidized to phosphoric acid or a phosphate.

1. Pb^{IV} becomes Pb'' in acid or alkaline mixture.
2. Ag' becomes Ag^0 in acid or alkaline mixture.
3. Hg'' becomes Hg' and then Hg^0 in acid or alkaline mixture.
4. As^V and As''' become As^0 in presence of **HCl**.
5. Bi''' becomes Bi^0 in presence of alkalis or acetic acid.
6. Cu'' becomes Cu_2H_2 and on boiling Cu^0 (separation from **Cd**).
7. Fe''' becomes Fe'', no action in alkaline mixture.
8. Cr^{VI} becomes Cr''', no action in alkaline mixture.
9. Co''' becomes Co'', no action in alkaline mixture.
10. Ni''' becomes Ni'', no action in alkaline mixture.
11. Mn''^{+n} becomes Mn'' in acid solution.
12. Mn^{IV+n} becomes Mn^{IV} in alkaline mixture.

B.—**With non-metals and their compounds.**

1. $H_3Fe(CN)_6$ becomes $H_4Fe(CN)_6$.
2. HNO_3 and HNO_2 become **NO**.
3. H_3PO_2 on heating becomes H_3PO_4 and PH_3.
4. H_2SO_3 becomes free sulphur with formation of some H_2S (Ponndorf, *J. C.*, 1877, **31**, 275).
   H_2SO_4 becomes first H_2SO_3 then **S**. See above.
5. **Cl** becomes **HCl** in acid mixture, a chloride with alkalis.
   HClO and $HClO_3$ form same products as **Cl**.
6. **Br** becomes **HBr** in acid mixture, a bromide with alkalis.
   $HBrO_3$ forms **HBr**.
7. **I** forms **HI**, in alkaline mixtures an iodide.
   HI, dry, reacts violently, forming H_3PO_3 and PH_4I (Ponndorf, *l. c.*).
   HIO_3 forms **HI**.

7. **Ignition.**—On ignition hypophosphites leave pyrophosphates, evolving PH_3. The acid decomposes on heating to PH_3 and H_3PO_4 (or HPO_3 if at a red heat).

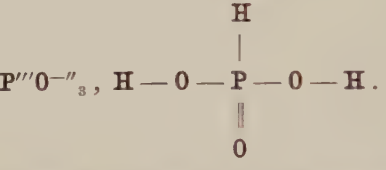
8. **Detection.**—Hypophosphorous acid may be known from phosphorous acid by adding cupric sulphate to the free acid and heating the solution to 55°. With hypophosphorous acid a reddish-black precipitate of copper hydride (Cu_2H_2) is thrown down, which, when heated in the liquid to 100°, is decomposed with the deposition of the metal and the evolution of hydrogen, whilst with phosphorous acid the metal is precipitated and hydrogen evolved, but no Cu_2H_2 is formed. Further, hypophosphorous acid reduces the permanganates immediately, but phosphorous acid only after some time. Phosphites precipitate barium, strontium, and calcium

salts, while hypophosphites do not. When hypophosphorous acid is treated with zinc and sulphuric acid it is converted into phosphoretted hydrogen. On boiling hypophosphorous acid with excess of alkali hydroxide, first a phosphite then a phosphate is formed, with evolution of hydrogen.

9. **Estimation.**— (1) By oxidation with nitric acid and then proceeding as with phosphoric acid. (2) By mercuric chloride acidulated with **HCl**: the temperature must not rise above 60°, otherwise metallic mercury will be formed. The precipitated **HgCl**, after washing and drying at 100°, is weighed.

$$NaH_2PO_2 + 4HgCl_2 + 2H_2O = 4HgCl + H_3PO_4 + NaCl + 3HCl$$

§253. Phosphorous acid. $H_3PO_3 = 82.064$.



$H'_3P'''0^{-''}_3$, $H-0-P(=0)-0-H$.

1. **Properties.**—Phosphorous anhydride, P_2O_3, is a snow-white solid, melting at 22.5°, and boiling at 173.1° (Thorpe and Tutton, *J. C.*, 1890, **57**, 545). The vapor density of the gaseous oxide indicates the molecule to be P_4O_6. *Specific gravity* of the liquid at 21°, 1.9431; of the solid at the same temperature, 2.135. It has an odor resembling that of phosphorus. Heated in a sealed tube at 200° it decomposes into P_2O_4 and **P** (T. and T., *J. C.*, 1891, **59**, 1019). It reacts slowly with cold water, forming H_3PO_3; with hot water the reaction is violent and PH_3 is evolved. Upon exposure to the air it oxidizes to P_2O_5.

The acid, H_3PO_3, is a crystalline solid, very deliquescent, melting at 74° (Hurtzig and Geuther, *A.*, 1859, **111**, 171). It is a dibasic acid, forming no tribasic salts (Amat, *C. r.*, 1889, **108**, 403). One or two of the hydrogen atoms are replaceable by metals forming acid or normal salts. The third hydrogen is never replaced by a metal, but may be replaced by organic radicles (Railton, *J. C.*, 1855, **7**, 216; Michaelis, *J. C.*, 1875, **28**, 1160). Neither meta nor pyrophosphorous acids are known, but a number of pyrophosphites have been prepared (Amat, *C. r.*, 1888, **106**, 1400; 1889, **108**, 1056; 1890, **110**, 1191 and 901; *A. Ch.*, 1891, (6), **24**, 289).

2. **Occurrence.**—Does not occur in nature.

3. **Formation.**—P_2O_3 is formed together with P_2O_5 when phosphorus is ignited in the air. H_3PO_3 is formed together with H_3PO_4 when phosphorus is oxidized with HNO_3; by the oxidation of H_3PO_2; by the action of **P** upon a concentrated solution of $CuSO_4$ in absence of air: $3CuSO_4 + P_4 + 6H_2O = Cu_3P_2 + 2H_3PO_3 + 3H_2SO_4$ (Schiff, *A.*, 1860, **114**, 200).

4. **Preparation.**—To prepare phosphorous anhydride, P_2O_3, phosphorus is burned in a tube with an insufficient supply of air (Thorpe and Tutton, *l. c.*). The acid, H_3PO_3, is prepared by dissolving the anhydride in cold water; by decomposing PCl_3 with water (Hurtzig and Geuther, *l. c.*).

5. **Solubilities.**—The acid is miscible in water in all proportions. Alkali phosphites are soluble in water, most others are insoluble (distinction from hypophosphites).

6. **Reactions.**—Phosphorous acid is a strong reducing agent, oxidizing to phosphoric acid when exposed to the air. It reduces salts of silver and gold to the metallic state and is changed to phosphoric acid by most of the strong oxidizing acids and by many of the higher metallic oxides. $HgCl_2$ becomes **HgCl** and then **Hg**°, $CuCl_2$ becomes **CuCl** then **Cu**° (Rammelsberg, *J. C.*, 1873,

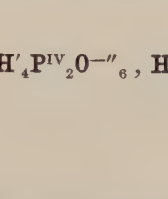
26, 13). Concentrated H_2SO_4 with heat forms H_3PO_4 and SO_2 (Adie, *J. C.*, 1891, **59**, 230). H_2SO_3 forms H_2S and H_3PO_4 (Woehler, *A.*, 1841, **39**, 252). Nascent hydrogen (Zn and H_2SO_4) produce PH_3 (Dusart, *C. r.*, 1856, **43**, 1126).

7. **Ignition.**—The acid is decomposed by ignition, forming HPO_3 and P or PH_3 (Vigier, *Bl.*, 1869, (2), **11**, 125; Hurtzig and Geuther, *l. c.*). Phosphites are decomposed by heat, leaving a pyrophosphate and a phosphide and evolving PH_3 or H (Rammelsberg, *B.*, 1876, **9**, 1577; and Kraut, *A.*, 1875, **177**, 274).

8. **Detection.**—By oxidation to H_3PO_4 and detection as such. It is distinguished from hypophosphorous acid by reducing $CuSO_4$ to Cu°, while the latter forms Cu_2H_2; also by the solubilities of the salts (§**252**, 8). Its reactions with oxidizing agents distinguish it with hypophosphorous acid from phosphoric acid.

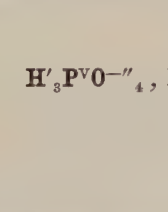
9. **Estimation.**—By oxidation to H_3PO_4 and estimation as such.

§254. Hypophosphoric acid. $H_4P_2O_6 = 162.112$.



Hypophosphoric acid is formed together with phosphorous and phosphoric acids by slowly oxidizing phosphorus in moist air (Salzer, *A.*, 1885, **232**, 114 and 271); also by oxidizing phosphorus with dilute HNO_3 in presence of silver nitrate (Philipp, *B.*, 1885, **18**, 749). It consists of small colorless hygroscopic crystals which melt at 55°. It decomposes when heated to 70° into H_3PO_3 and HPO_3, and at 120° gives $H_4P_2O_7$ and PH_3 (Joly, *C. r.*, 1886, **102**, 110 and 760). It is oxidized to H_3PO_4 by warm HNO_3, slowly by $KMnO_4$ in the cold, rapidly when heated. It is not oxidized by H_2O_2, chlorine water or H_2CrO_4; $HgCl_2$ becomes HgCl (Amat, *C. r.*, 1890, **111**, 676). It is not reduced by Zn and H_2SO_4 (distinction from H_3PO_2 and H_3PO_3). With a solution of silver nitrate it gives a white precipitate which does not blacken in the light (distinction from H_3PO_2 and H_3PO_3). It forms four series of salts, all four hydrogen atoms being replaceable by a metal. The hypophosphates are much more stable towards oxidizing agents than hypophosphites or phosphites.

§255. Phosphoric acid. $H_3PO_4 = 98.064$.



1. **Properties.**—Phosphoric anhydride, P_2O_5 *, is a white, flakey, very deliquescent solid, fusible, subliming undecomposed at a red heat. It is very soluble in water, forming three varieties of phosphoric acid: *ortho*, H_3PO_4; *meta*, HPO_3;

* According to Tilden and Barnett (*J. C.*, 1896, **69**, 154) the molecule is P_4O_{10} not P_2O_5; P_4O_6 not P_2O_3 (Thorpe and Tutton, *J. C.*, 1891, **59**, 1022); and P_4S_6 not P_2S_3 (Isambert, *C. r.*, 1886, **102**, 1386).

and *pyro*, $H_4P_2O_7$. Orthophosphoric acid is a translucent, feebly crystallizable and very deliquescent soft solid. *Specific gravity*, 1.88 (Schiff, *A.*, 1860, **113**, 183); *melting point*, 41.75° (Berthelot, *Bl.*, 1878, (2), **29**, 3). It is changed by heat, first to pyrophosphoric acid, then to metaphosphoric acid. Orthophosphoric acid forms three classes of salts: $M'H_2PO_4$, primary, monobasic or monometallic phosphates; M'_2HPO_4, secondary, dibasic or dimetallic phosphates; and M'_3PO_4, tertiary, tribasic, trimetallic or normal phosphates. The first two are acid salts, but Na_2HPO_4 is alkaline to test paper. Metaphosphoric acid, HPO_3, $H - O - \underset{\underset{O}{\|}}{P} = O$, is a white waxy solid, volatile at a red heat (ordinary glacial phosphoric acid owes its hardness to the universal presence of sodium metaphosphate). It is a monobasic acid, but there are various polymeric modifications, distinguished from each other chiefly by physical differences of the acids and their salts (Tammann, *Z. phys. Ch.*, 1890, **6**, 122).

Pyrophosphoric acid, $H_4P_2O_7$, $H - O - \overset{\overset{O}{\|}}{\underset{\underset{\underset{H}{|}}{O}}{P}} - O - \overset{\overset{O}{\|}}{\underset{\underset{\underset{H}{|}}{O}}{P}} - O - H$, is a glass-like solid (Peligot, *A. Ch.*, 1840, (2), **73**, 286), very soluble in, but unchanged by, water at ordinary temperature; changed by boiling water to H_3PO_4. Heated to redness HPO_3 is formed. It forms two classes of salts: $M'_2H_2P_2O_7$ and $M'_4P_2O_7$.

2. **Occurrence.**—Phosphates of **Al**, **Ca**, **Mg** and **Pb** are widely distributed in minerals. Guano consists quite largely of calcium phosphate. Calcium and magnesium phosphates are found in the bones of animals and in the ashes of plants. The free acids are not found in nature.

3. **Formation.**—*Phosphoric anhydride*, P_2O_5, is formed by burning phosphorus in great excess of air; also by burning phosphorus in **NO**, NO_2, or ClO_2. *Orthophosphoric acid*, H_3PO_4, is formed by long exposure of phosphorus to moist air, or by oxidation with HNO_3; by oxidation of H_3PO_2 or H_3PO_3 with the halogens, HNO_3, $HClO_3$, etc.; by treating P_2O_5, HPO_3, or $H_4P_2O_7$ with boiling water; by combustion of PH_3 in moist air; and by action of water on PCl_5. It is also formed from metallic phosphates by transposition with acids in cases where a precipitate results, as a lead or barium phosphate with sulphuric acid, or silver phosphate with hydrochloric acid. But when the products are all soluble, as calcium phosphate with acetic acid or sodium phosphate with sulphuric acid, the transposition is only partial; so that unmixed phosphoric acid is not obtained. A non-volatile acid, like phosphoric, is not separated from liquid mixtures, as the volatile acids are, like hydrochloric. The change represented by equation (*a*) can be verified, that is, pure phosphoric acid can be separated; but the changes shown in equations (*b*) and (*c*) do not comprise the whole of the material taken. In the operation (*b*) some sodium phosphate and some nitric acid will be left, and in (*c*) some trihydrogen phosphate will no doubt be made.

$$a.\quad CaH_4(PO_4)_2 + H_2C_2O_4 = CaC_2O_4 + 2H_3PO_4$$
$$b.\quad Na_2HPO_4 + 2HNO_3 = 2NaNO_3 + H_3PO_4$$
$$and\quad Na_2HPO_4 + HNO_3 = NaNO_3 + NaH_2PO_4$$
$$c.\quad 2CaHPO_4 + 2HCl = CaCl_2 + CaH_4(PO_4)_2$$

Metaphosphoric acid is formed by treating P_2O_5 with cold water; by decomposition of lead metaphosphate with H_2S or of the barium salt with H_2SO_4; by ignition to dull redness of phosphorus or any of its acids in the presence of air and moisture.

Pyrophosphoric acid, $H_4P_2O_7$, is formed by the decomposition of lead pyrophosphate, $Pb_2P_2O_7$, with H_2S or of the corresponding barium salt with H_2SO_4; or by heating H_3PO_4 to a little above 200° until no yellow silver phosphate, Ag_3PO_4, is obtained on dissolving in water and treatment with silver nitrate after neutralization with NH_4OH.

4. **Preparation.**—To prepare P_2O_5, phosphorus is burned in a slow current of dry oxygen heating to about 300°, then in a more rapid current of the gas, and finally the P_2O_5 is distilled in an atmosphere of oxygen (Shenstone, *Watts' Dic.*, 1894, **IV,** 141). H_3PO_4 is prepared by warming phosphorus, one part, with nitric acid, *sp. gr.* 1.20, ten to twelve parts, with addition of 300 to 600 milligrams of iodine to 100 grams of phosphorus, until the phosphorus is completely dissolved. The excess of HNO_3 is removed by evaporation, water is added and the solution is saturated with H_2S to remove any arsenic that may be present. The solution is then evaporated to a syrupy consistency at temperatures not above 150° (Krauthausen, *Arch. Pharm.*, 1877, **210,** 410; Huskisson, *B.*, 1884, **17,** 161). Many *orthophosphates* are formed by the action of H_3PO_4 upon metallic oxides or carbonates; by the reaction between an alkali phosphate and a soluble salt of the heavy metal; by fusion of a metaphosphate with the corresponding metallic oxide or hydroxide; also by long continued boiling of meta or pyrophosphates. *Metaphosphates* are formed by double decomposition with $NaPO_3$ or by fusion of a monobasic phosphate or any phosphate having but one hydrogen equivalent substituted for a metal, the oxide of which is non-volatile, *e. g.*, $NaNH_4HPO_4$. *Pyrophosphates* are formed by double decomposition with $Na_4P_2O_7$; by action of $H_4P_2O_7$ on certain oxides or hydroxides; also by ignition of dibasic orthophosphates, *e. g.*, Na_2HPO_4. $Na_2H_2P_2O_7$ may be prepared by titrating a saturated solution of $Na_4P_2O_7$ with HNO_3 until the solution gives a red color with methyl orange. Upon standing the salt separates in large crystals (Knorre, *Z. angew.*, 1892, 639).

5. **Solubilities.**—All the phosphoric acids are readily soluble in water, as are all alkali phosphates. Alkali primary orthophosphates have an acid reaction in their solutions; alkali secondary and tertiary phosphates are alkaline in their solutions; the latter is easily decomposed, even by CO_2, forming the secondary salt. A number of non-alkali primary orthophosphates are soluble in water, *e. g.*, $CaH_4(PO_4)_2$. All normal and dimetallic orthophosphates are insoluble except those of the alkalis. The normal and dimetallic phosphates of the alkalis precipitate solutions of all other salts. The precipitate is a normal, dimetallic, or basic phosphate, except that with the chlorides of mercury and antimony it is not a phosphate but an oxide or an oxychloride.

All phosphates are dissolved or transposed by HNO_3, HCl, or H_2SO_4, and all are dissolved by $HC_2H_3O_2$ except those of Pb, Al and Fe'''. All are soluble in H_3PO_4 except those of lead, tin, mercury, and bismuth.

The non-alkali meta and pyrophosphates are generally insoluble in water. The *pyrophosphates of the alkaline earth metals* are difficultly soluble in acetic acid. The most of the pyrophosphates of the heavy metals,

except silver, are soluble in solutions of alkali pyrophosphates, as *double pyrophosphates soluble* in water (distinction from orthophosphates). Ferric iron as a double pyrophosphate loses the characteristic properties of that metal (Persoz, *J. C.*, 1849, **1**, 183). Phosphates are insoluble in alcohol.

6. **Reactions.**—*A.*—**With metals and their compounds.**—Phosphoric acid dissolves some metals, *e. g.*, **Fe**, **Zn** and **Mg** with evolution of hydrogen. It unites with the oxides and hydroxides of the alkalis and alkaline earths and with other freshly precipitated oxides and hydroxides except perhaps antimonous oxide. It also decomposes all carbonates evolving CO_2. Phosphates are formed in the above reactions, the composition of which depends upon the conditions of the experiment.

Free orthophosphoric acid is not precipitated by ordinary salts of third, fourth and fifth group metals (in instance of ferric chloride, a distinction from pyrophosphoric acid and metaphosphoric acid).* but is precipitated in part by silver nitrate, and lead nitrate and acetate. **Ammoniacal solution of calcium chloride** or of barium chloride precipitates the normal phosphate.

Free metaphosphoric acid precipitates solutions of silver nitrate, lead nitrate, and lead acetate, the precipitates being insoluble in excess of metaphosphoric acid, and soluble in moderately dilute nitric acid. Barium, calcium and ferrous chlorides, and magnesium, aluminum, and ferrous sulphates, are not precipitated by free metaphosphoric acid. Ferric chloride is precipitated, a distinction from orthophosphoric acid.

Free pyrophosphoric acid gives precipitates with solutions of silver nitrate, lead nitrate or acetate, and ferric chloride; no precipitates with barium or calcium chloride, or with magnesium or ferrous sulphate.

Orthophosphoric acid—or an orthophosphate with acetic acid—*does not coagulate* egg **albumen** or **gelatine**. This is a distinction of both orthophosphoric acid and pyrophosphoric acid *from metaphosphoric acid*.

With **silver nitrate** soluble orthophosphates in neutral solution form silver orthophosphate, Ag_3PO_4, yellow; with metaphosphates, silver metaphosphate, $AgPO_3$, white; and with pyrophosphates, silver pyrophosphate, $Ag_4P_2O_7$, white, all soluble in ammonium hydroxide. Silver metaphosphate is soluble in excess of an alkali metaphosphate (distinction from pyrophosphates).

If a disodium or dipotassium orthophosphate is added to solution of silver nitrate, free acid is formed, and an acid reaction to test-paper is induced (*a*). But with a trisodium or tripotassium phosphate, the solution remains neutral (*b*)—*a means of distinguishing the acid phosphates from the normal.*

(*a*) $Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + 2NaNO_3 + HNO_3$

(*b*) $Na_3PO_4 + 3AgNO_3 = Ag_3PO_4 + 3NaNO_3$

Free orthophosphoric acid forms no precipitate with reagent silver nitrate, because silver phosphate is soluble in dilute HNO_3.

With **lead acetate** or nitrate, Na_2HPO_4 forms Pb_3PO_4, white, insoluble in acetic acid, as are also the phosphates of aluminum and ferricum. With

* A solution containing 5 p. c. *ferric chloride*, mixed with one-fourth its volume of a 10 p. c. solution of *orthophosphoric* acid, requires that near half of the latter be neutralized (so that phosphate is to phosphoric acid as 1.114 is to 1.000) before precipitation occurs. On the other hand, 4 cc. of a 5 p. c. solution of ferric chloride, mixed with 1 cc. of a 6 p. c. solution of *metaphosphoric* acid, form a precipitate, to dissolve which, 20 cc. of the same metaphosphoric acid solution or 5 cc. of a 24 p. c. solution of hydrochloric acid are required. Four cc. of a 5 p. c. solution of *silver nitrate* with 1 cc. of a 10 p. c. solution of *orthophosphoric* acid give a precipitate, to dissolve which requires 7 cc. of the same orthophosphoric acid solution. [The Author's report of work by Mr. Morgan, *Am. Jour. Phar.*, 1876, **48**, 534. Kratschmer and Sztankovansky, *Z.*, 1883, **21**, 520.]

$PbCl_2$ the precipitate always contains a chloride. Free phosphoric acid, H_3PO_4, forms an acid phosphate, $PbHPO_4$ (Heintz, *Pogg.*, 1848, **73**, 119). Lead salts also form white precipitates with soluble pyro and metaphosphates; the pyro salt, $Pb_2P_2O_7$, is soluble in an excess of $Na_4P_2O_7$. Bismuth salts form $BiPO_4$, insoluble in dilute HNO_3.

Solutions of orthophosphates give, with soluble **ferric, chromic,** and **aluminum** salts, mostly the normal *phosphates*, $FePO_4$, etc. The *ferric phosphate* is but slightly soluble in acetic acid, and for this reason it is made the *means of separating phosphoric acid from metals* of the earths and alkaline earths (§**152**). Solution of sodium or potassium acetate is added; and if the reaction is not markedly acid, it is made so by addition of acetic acid. Ferric chloride (if not present) is now added, drop by drop, avoiding an excess. The precipitate, *ferric phosphate*, is brownish-white.

With **zinc** and **manganous** salts, the precipitate is dimetallic or normal—$ZnHPO_4$, or $Zn_3(PO_4)_2$—according to the conditions of precipitation. When a manganic compound is mixed with aqueous **phosphoric acid**, the solution evaporated to dryness and gently ignited, a violet or deep blue mass is obtained, from which water dissolves a purple-red *manganic hydrogen phosphate*, a distinction from manganous compounds. With salts of nickel, a light green normal phosphate is formed; with cobalt, a reddish normal phosphate.

Soluble salts of the **alkaline earth metals,** with **dimetallic** alkali phosphates, as Na_2HPO_4, form white precipitates of *phosphates, two-thirds metallic*, as $CaHPO_4$; with **trimetallic** alkali phosphates, white precipitates of *phosphates, normal* or full metallic, as $Ca_3(PO_4)_2$. The precipitates are soluble in acetic acid, and in the stronger acids. Concerning the ammonium magnesium phosphate, see §**189**, *6d*.

Magnesium salts with ammonium hydroxide give a precipitate of double *pyrophosphate*, soluble in alkali pyrophosphate solution.

Magnesium salts with ammonium hydroxide are not precipitated by soluble metaphosphates unless very concentrated.

Ammonium molybdate, in its nitric acid solution (§**75**, *6d*), furnishes an exceedingly delicate test for phosphoric acid, giving the pale yellow precipitate, termed *ammonium phosphomolybdate*. The molybdate should be in excess, therefore it is better to add a little of the solution tested (which must be neutral or acid) to the reagent, taking a half to one cc. of the latter in a test-tube. For the full delicacy of the test, it should be set aside, at 30° to 40°, for several hours.

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 = (NH_4)_3PO_4.12MoO_3 + 21NH_4NO_3 + 12H_2O.$$

Ammonium molybdate reacts but slowly with meta or pyrophosphate solutions—and not until orthophosphoric acid is *formed by digestion with the nitric acid* of the reagent solution.

B.—**With non-metals and their compounds.**—Phosphoric acid is not reduced by any of the reducing acids. Phosphates of the first two groups are transposed by H_2S, and of the first four groups by alkali sulphides with formation of a sulphide of the metal, except **Al** and **Cr**, which form a hydroxide; phosphoric acid or an alkali phosphate is also formed. **HCl**, HNO_3, and H_2SO_4 transpose all phosphates and all are transposed by acetic acid except those of **Pb**, **Al** and **Fe'''** phosphates. Sulphurous acid transposes the phosphates of **Ca**, **Mg**, **Mn**, **Ag**, **Pb**, and **Ba**, also the arsenite and arsenate of calcium (Gerland, *J. C.*, 1872, **25**, 39). Excess of phosphoric acid completely displaces the acid of all nitrates, chlorides, and sulphates upon evaporation and long-continued heating on the sand bath.

7. **Ignition with metallic magnesium** (or sodium) reduces phosphorus from phosphates to magnesium *phosphide*, P_2Mg_3, recognized by odor of PH_3, formed on contact of the phosphide with water. A bit of magnesium wire (or of sodium) is covered with the previously ignited and powdered substance in a glass tube of the thickness of a straw, and heated. If any combination of phosphoric acid is present, vivid incandescence will occur, and a black mass will be left. The latter, crushed and wet with water, gives the odor of phosphorus hydride.

Orthophosphoric acid heated to 213° forms pyrophosphoric acid; when heated to dull redness the meta acid is obtained, which sublimes upon further heating without change. Phosphoric anhydride, P_2O_5, cannot be prepared by ignition of phosphoric acid. Tribasic orthophosphates, normal pyrophosphates, and metaphosphates of metals whose oxides are not volatile and not decomposed by heat alone are unchanged upon ignition. Dimetallic orthophosphates, M'_2HPO_4, are changed to normal pyrophosphates upon ignition; also tribasic orthophosphates when one-third of the base is volatile, *e.g.*, $MgNH_4PO_4$. Mono-metallic or primary orthophosphates, $M'H_2PO_4$, become metaphosphates; also secondary or tertiary orthophosphates when only one atom of hydrogen is displaced by a metal whose oxide is non-volatile, *e.g.*, $NaNH_4HPO_4$. Acid pyrophosphates, $M'_2H_2P_2O_7$, form metaphosphates. When meta or pyrophosphates are fused with an excess of a non-volatile oxide, hydroxide or carbonate the tertiary orthophosphate is formed (*Watts'*, 1894, **IV**, 106).

Phosphates of **Al**, **Cr**, **Fe**, **Cu**, **Co**, **Ni**, **Mn**, **Gl** and **U** when heated to a white heat with an alkali sulphate form oxides of the metals and an alkali tribasic orthophosphate; phosphates of **Ba**, **Sr**, **Ca**, **Mg**, **Zn** and **Cd** form double phosphates, partial transposition taking place (Derome, *C. r.*, 1879, **89**, 952; Grandeau, *A. Ch.*, 1886, (6), **8**, 193).

8. **Detection.**—The presence of orthophosphoric acid in neutral or acid solutions is detected by the use of an excess of an ammonium molybdate solution (§**75**, *6d*). With pyro and metaphosphoric acids no reaction is obtained except as they are changed to the ortho **acid** by the reagents used. Disodium phosphate, Na_2HPO_4, after precipitation with silver nitrate, reacts acid to test papers. With trisodium phosphate the solution is neutral (distinction). Orthophosphates are distinguished from pyro and metaphosphates by the color of the precipitate with silver nitrate: Ag_3PO_4 is yellow, $Ag_4P_2O_7$ and $AgPO_3$ are white. Also by the fact that only the ortho acid is precipitated by ammonium molybdate. Nearly all pyrophosphates are soluble in sodium pyrophosphate, $Na_4P_2O_7$ (distinc-

tion from orthophosphates). Hager (*J. C.*, 1873, **26,** 940) gives a method for detecting the presence of H_3PO_3, H_3AsO_3, or HNO_3 in H_3PO_4. Sodium metaphosphate does not give a precipitate with $ZnSO_4$ cold and in excess; with $Na_4P_2O_7$ and $Na_2H_2P_2O_7$ a white precipitate of $Zn_2P_2O_7$ is obtained (Knorre, *Z. angew.*, 1892, 639).

9. **Estimation.**—(*a*) By precipitation as magnesium ammonium phosphate, $MgNH_4PO_4$, and ignition to the pyrophosphate. (*b*) By precipitation and weighing as lead phosphate, $Pb_3(PO_4)_2$. (*c*) By precipitation from neutral or acid solution by ammonium molybdate and after drying at 140° weighing as ammonium phosphomolybdate. Consult Janovsky (*J. C.*, 1873, **26,** 91) for a review of all the old methods.

§256. Sulphur. S = 32.06. Usual valence two, four and six (§14).

1. **Properties.**—Sulphur is a solid, in yellow, brittle, friable masses (from *melting*); or in yellowish, gritty powder (from *sublimation*) or in nearly white, slightly cohering, finely crystalline powder (by *precipitation* from its compounds). At —50° it is white (Schoenbein, *J. pr.*, 1852, **55,** 161). The *specific gravity* of native sulphur is 2.0748 (Pisati, *B.*, 1874, **7,** 361). *Melting point* rhombic 114.5°. *Boiling point*, 444.53° (Callendar and Griffiths, *C. N.*, 1891, **63,** 2). *Vapor density* at 1160° is 34, indicating that the molecule is S_2 (Bineau, *C. r.*, 1859, **49,** 799); but at lower temperatures the molecule seems to vary from S_2 to S_8. Sulphur is polymorphous, existing in various crystalline forms, rhombic, monoclinic and triclinic systems, and also in amorphous conditions. It is also classified by the relative solubilities of the various forms in carbon disulphide. In chemical activity, volatility and other properties it stands as the second member of the Oxygen Series: **O,** 16,000; **S,** 32.07; **Se,** 79.2; and **Te,** 127.5. On being heated it melts at 114.5° to a pale yellow liquid; as the temperature rises it grows darker and thicker, until at about 180° it is nearly solid, so that the dish may be inverted without spilling. At 260° it again becomes a liquid as at first; and at 444.53° it boils and is converted into a brownish-red vapor. If it is slowly cooled, exactly the same physical changes take place in the reverse order, becoming thick at 180° and thin again at 114.5°, and at lower temperatures solid. If, at a temperature near its boiling point, it is poured into cold water, it forms a soft, ductile, elastic string, resembling india-rubber. In a few hours this ductile sulphur changes back to the ordinary form, the change evolving heat. But if poured into water from the other liquid form—that is, at 114.5°—it forms only ordinary, brittle sulphur. In contact with air sulphur ignites at 248° (Hill, *C. N.*, 1890, **61,** 125); burning in air or oxygen with a pale blue flame and penetrating odor to SO_2.

The isolated oxides of sulphur are SO_2, SO_3, S_2O_3 and S_2O_7. Sulphur and oxygen combine directly to form SO_2 and SO_3; the former by burning sulphur in oxygen, the latter by the action of ozone upon SO_2; also by burning sulphur with oxygen under several atmospheres pressure. S_2O_3 is made by dissolving sulphur in sulphur dioxide; S_2O_7 by the action of the electric discharge upon a mixture of SO_3 and **O**.

2. **Occurrence.**—(*a*) Found in a free state, and as SO_2 in volcanic districts. (*b*) As H_2S in some mineral springs. (*c*) As a sulphide: iron pyrites, FeS_2; copper pyrites, $CuFeS_2$; orpiment, As_2S_3; realgar, As_2S_2; zinc blende, **ZnS**; cinnabar, **HgS**; galena, **PbS**. (*d*) As a sulphate: gypsum, $CaSO_4.2H_2O$; heavy spar, $BaSO_4$; kieserite, $MgSO_4.H_2O$; bitter spar (Epsom salts), $MgSO_4.7H_2O$; Glauber salt, $Na_2SO_4.10H_2O$, etc.

3. **Formation.**—(*a*) By decomposing polysulphides with **HCl** (Schmidt, *Pharmaceutische Chemie*, 1898, 175). (*b*) By adding an acid to a solution of a thiosulphate. (*c*) By the reaction between SO_2 and H_2S: $2SO_2 + 4H_2S = 3S_2 + 4H_2O$. (*d*) By the decomposition of metallic sulphides with nitric acid: $2Bi_2S_3 + 16HNO_3 = 4Bi(NO_3)_3 + 3S_2 + 4NO + 8H_2O$.

4. **Preparation.**—(*a*) The native sulphur is separated from the clay and rock in which it is embedded, partly by melting and partly by distillation. (*b*) From FeS_2 by heating in close cylinders $3FeS_2 = Fe_3S_4 + S_2$; or at a higher temperature: $2FeS_2 = 2FeS + S_2$. Much of the sulphur contained in pyrites is converted into and utilized as sulphuric acid.

5. **Solubilities.**—Ordinary (**not precipitated**) sulphur is soluble in carbon disulphide; the ductile variety is insoluble. There are several allotropic forms of sulphur. Samples of commercial sulphur are almost never found which are entirely soluble or insoluble in carbon disulphide. Forms of sulphur insoluble in CS_2 are changed to soluble forms upon heating to the melting point; also amorphous sulphur insoluble in CS_2 (formed by adding acids to thiosulphates or SO_2 to H_2S) is changed to the soluble form by mixing with a solution of H_2S in water. It dissolves readily in hot solutions of the hydroxides of potassium, sodium, calcium or barium, forming polysulphides and thiosulphates: $3Ca(OH)_2 + 6S_2 = 2CaS_5 + CaS_2O_3 + 3H_2O$. These can be separated by alcohol, in which the sulphides dissolve. These products are also readily decomposed by acids with separation of sulphur (method of preparation of precipitated sulphur).

Precipitated sulphur (in analysis, HCl upon $(NH_4)_2S_x$) is soluble in benzol or low boiling petroleum ether; of value in analysis for the removal of the sulphur to detect the presence of traces of As or Sb sulphides (Fresenius, *Z.*, 1894, **33**, 573).

6. **Reactions.** *A.*—**With metals and their compounds.**—Sulphur does not combine with metals without the aid of heat (see 7), except that under very great pressure (6500 atmospheres) it combines with Pb, Sn, Sb, Bi, Cu, Cd, Fe, Zn, and Mg (Spring, *B.*, 1883, **16**, 999).

Flowers of sulphur boiled with $SnCl_2$ gives SnS and $SnCl_4$; with $HgNO_3$ almost exactly one-half of the mercury is precipitated as HgS. No action with sulphates of Cd, Fe″, Mn″, Ni and Zn; with acid solutions of $SbCl_3$ and $BiCl_3$; or with solutions of As^V and As‴ (Vortmann and Padberg, *B.*, 1889, **22**, 2642). Sulphur boiled with hydroxides of K, Na, NH_4, Ba, Ca, Sr, Mg, Co, Ni, Mn, Hg″, Bi, Cu′, Cu″, Cd, Pb, Ag, and Hg′ forms sulphides and thiosulphates; also some sulphates are formed. No action with hydroxides of Fe, Zn and Sn (Senderens, *Bl.*, 1891, (3), **6**, 800).

B.—**With non-metals and their compounds.**

1. HCN warmed with sulphur or a polysulphide becomes a thiocyanate: $2KCN + S_2 = 2KCNS$ or $4HCN + 2(NH_4)_2S_4 = 4NH_4CNS + 2H_2S + S_2$.

2. HNO_3 becomes NO and H_2SO_4. Strong acid and long continued boiling are necessary to the complete oxidation of the sulphur. The crystallized variety is attacked with much greater difficulty than the amorphous or flowers (Saint-Gilles, *A. Ch.*, 1858, (3), **54**, 49).

3. Red phosphorus combines readily at ordinary temperature, forming P_2S_3 or P_2S_5, depending upon the relative amounts of the elements used. Ordinary phosphorus combines explosively. See §252, 6. Tribasic sodium or potassium phosphate when boiled with sulphur forms alkali polysulphide and thiosulphate, changing the phosphate to dibasic phosphate (Filhol and Senderens, *C. r.*, 1883, **96**, 1051).

4. H_2SO_4, concentrated and hot, becomes SO_2 from both the **S** and the H_2SO_4: $4H_2SO_4 + S_2 = 6SO_2 + 4H_2O$. SO_3 when added to **S** at 12° forms the blue hyposulphurous anhydride, S_2O_3 (not the anhydride of thiosulphuric acid, S_2O_2). SO_2 reacts with **S** even at ordinary temperatures, forming thiosulphuric acid and tri or tetrathionic acid (Colefax, *J. C.*, 1892, **61**, 199).

5. **Cl** in presence of water forms **HCl** and H_2SO_4. $HClO_3$ becomes **HCl** and H_2SO_4.

6. **Br** in presence of water becomes **HBr** and H_2SO_4. $HBrO_3$ becomes **HBr** and H_2SO_4.

7. Sulphur does not appear to have any action upon iodine or upon iodine compounds.

7. **Ignition.**—**In the air**, at ordinary temperatures, finely divided sulphur is very slightly oxidized, by ozone, to *sulphuric acid*; at 248° it begins to oxidize rapidly to *sulphurous anhydride*, burning with a blue flame.

Sulphur, when fused with the following elements, combines with them to form sulphides: **Pb**, **Ag**, **Hg**, **Sn**, **As**, **Sb**, **Bi**, **Cu**, **Cd**, **Zn**, **Co**, **Ni**, **Fe**, **Sr**, **Ca**, **Mg**, **K**, **Na**, **In**, **Tl**, **Pt**, **Pd**, **Rh**, **Ir**, **Li**, **Ce**, **La**, **Ne**, **Pr**.

S^{VI-n} becomes S^{VI} when fused with alkaline carbonate and nitrate or chlorate. That is, free sulphur, **S°**, or any compound containing sulphur with valence less than six, is oxidized to a sulphate if fused with an alkaline nitrate or chlorate, nitric oxide or a chloride being formed and carbon dioxide escaping.

8. **Detection.**—(*a*) By burning in the air to a gas having the odor of burning matches. (*b*) By its solubility in CS_2. (*c*) By formation of H_2SO_4 with oxidizing agents. (*d*) By the formation of sulphides upon fusion with metals. (*e*) By the blackening of silver coin after boiling with alkali hydroxide. (*f*) Formation of reddish-purple with sodium nitroferricyanide after boiling with alkali hydroxide. (*g*) In organic compounds by heating with **Na** and testing the Na_2S with sodium nitroferricyanide (Vohl, *B.*, 1876, **9**, 875).

9. **Estimation.**—Sulphur is usually estimated by oxidation to a sulphate and weighing as $BaSO_4$.

§257. Hydrosulphuric acid. $H_2S = 34.076$.

$H'_2S^{-''}$, $H-S-H$.

1. **Properties.**—*Molecular weight*, 34.076. *Vapor density*, 17. *Boiling point*, —61.8°. *Freezing point*, —85.56°. Under a pressure of 14.6 atmospheres it becomes a liquid at 11.11° (Faraday, *A.*, 1845, **56**, 156). It is a colorless poisonous gas. It burns readily, forming sulphur dioxide and water: $2H_2S + 3O_2 = 2SO_2 + 2H_2O$. The aqueous solution slowly decomposes upon exposure to the air with separation of sulphur. The gas is readily expelled from its aqueous solution by boiling; slowly when exposed at ordinary temperature. Both the gas and the water solutions have a feebly acid reaction towards moist litmus paper. They also possess a strong characteristic odor, resembling that of rotten eggs. In acid or in alkaline solutions it is a strong reducing agent. See 6.

2. **Occurrence.**—Found free in volcanic gases and frequently in mineral springs. While the inhaled gas is poisonous, the mineral waters containing it are reputed to be a healthful beverage.

3. **Formation of Hydrosulphuric Acid.**—(*a*) By direct union of the elements when passed over pumice stone heated to 400° (Corenwinder, *A. Ch.*, 1852, (3), **34**, 77). (*b*) Heating paraffin or tallow with sulphur (Fletcher, *C. N.*, 1879, **40**, 154); and by passing illuminating gas through boiling sulphur (Taylor, *C. N.*, 1883, **47**, 145). (*c*) The sulphur in coal becomes H_2S in the process of gas-making. (*d*) From steam and sulphur at 440°. (*e*) Often occurs in nature from reduction of gypsum by decaying organic matter (Myers, *J. pr.*, 1869, **108**, 123). (*f*) Transposition of sulphides by hydracids or by dilute phosphoric or dilute sulphuric acid. (*g*) Decomposition of organic compounds containing sulphur.

Formation of Sulphides.—(*1*) By fusion of the metals with sulphur, see §256, 7. (*2*) By action of H_2S upon the free metals, hydrogen being evolved. With **Hg** and **Ag** this occurs at ordinary temperature, but with most metals a higher temperature is needed. (*3*) Action of H_2S on metallic oxides or hydroxides. Those sulphides which are decomposed by water (*e. g.*, Al_2S_3, Cr_2S_3) are not formed in its presence, but by action of H_2S upon the oxide at a red heat. (*4*) By action of soluble sulphides upon metallic solutions. The ordinary sulphides of the first four groups are formed thus, except ferric salts, which are precipitated as **FeS**, and aluminum and chromic salts as hydroxides. (*5*) By action of CS_2 upon oxides at a red heat. (*6*) By action of free sulphur upon oxides at a red heat. (*7*) By the action of charcoal upon the oxyacids of sulphur at a red heat in presence of an alkaline carbonate. To prepare a sulphide absolutely arsenic free, take $BaSO_4$, 100 grams; coal, pulverized, 25 grams; and **NaCl**, 20 grams, mix, ram into a clay crucible and ignite to a white heat for several hours (Winkler, *Z.*, 1888, **27**, 26). (*8*) By the action of zinc amalgam on sulphuric acid (Walz, *C. N.*, 1871 **23**, 245). (*9*) As a reagent for the formation of metallic sulphides in analysis it is recommended by Schiff and Tarugi (*B.*, 1894, **27**, 3437), Schiff (*B.*, 1895, **28**, 1204), and Tarugi (*Gazzetta*, 1895, **25**, i, 269), to use ammonium thioacetate, CH_3COSNH_4; prepared by distilling a mixture of phosphorus pentasulphide and glacial acetic acid (300 grams each) with 150 grams of cracked glass. A large distilling flask is used and the distillate is collected to 103°. It is then dissolved in a slight excess of ammonium hydroxide, diluting to three volumes from one volume of the acid. Salts of the metals of the first two groups in acid solution are readily precipitated as sulphides upon warming with this reagent.

1. $2Fe + S_2 = 2FeS$
2. $2Ag + H_2S = Ag_2S + H_2$
3. $Pb(OH)_2 + H_2S = PbS + 2H_2O$
   $4Fe(OH)_3 + 6H_2S = 4FeS + S_2 + 12H_2O$
4. $4FeCl_3 + 6(NH_4)_2S = 4FeS + S_2 + 12NH_4Cl$
5. $2CaO + CS_2 = 2CaS + CO_2$
6. $4CaO + 3S_2 = 4CaS + 2SO_2$
7. $K_2SO_4 + 2C = K_2S + 2CO_2$

4. **Preparation.**—For laboratory purposes it is nearly always made by adding H_2SO_4 or **HCl** to **FeS**. The ferrous sulphide is prepared either by fusion of the iron with the sulphur, or by bringing red hot iron rods in contact with sticks of sulphur, and is made to drop into tubs of cold water. Dilute H_2SO_4 should be used:* $FeS + H_2SO_4 = FeSO_4 + H_2S$. Concentrated H_2SO_4 has no action on **FeS**, unless heated and then SO_2 is evolved: $2FeS + 10H_2SO_4 = Fe_2(SO_4)_3 + 9SO_2 + 10H_2O$; and frequently free sulphur is formed by the action of the H_2S upon the SO_2 first formed.

* If the acid is diluted with eleven volumes of water ferrous sulphate crystals will not be deposited.

The colorless **ammonium sulphide,** $(NH_4)_2S$, is prepared by saturating ammonium hydroxide with H_2S until a sample will no longer give a precipitate with a solution of magnesium sulphate; showing that ammonium hydroxide is no longer present. Upon standing the solution gradually becomes yellow with formation of the *polysulphides* or **yellow ammonium sulphide,** $(NH_4)_2S_x$. This may be hastened by the addition of sulphur (Bloxam, *J. C.*, 1895, **67,** 277).

Sodium sulphide, Na_2S, is prepared by neutralizing an alcoholic solution of **NaOH** with H_2S and then adding an equal amount of **NaOH** and allowing to crystallize; air being excluded. The various polysulphides, Na_2S_2 to Na_2S_5, are prepared by boiling the normal sulphide with the calculated amounts of sulphur (Boettger, *A.*, 1884, **223,** 335; Geuther, *A.*, 1884, **224,** 201).

5. **Solubilities.**—At 15° *water* dissolves 2.66 volumes of the gas H_2S.

Sulphides which dissolve in dilute H_2SO_4 evolve H_2S, *e. g.*, **CdS**, **FeS**, **MnS**, **ZnS**, etc. But if a sulphide requires concentrated H_2SO_4 for its solution; **S** and SO_2 are formed or SO_2 alone; *e. g.*, Bi_2S_3, **CuS**, **HgS**. If concentrated H_2SO_4 be used upon a sulphide that might have been dissolved in the dilute acid, then no H_2S is evolved: $ZnS + 4H_2SO_4 = ZnSO_4 + 4SO_2 + 4H_2O$. Or with a small amount of water present: $2ZnS + 4H_2SO_4 = 2ZnSO_4 + S_2 + 2SO_2 + 4H_2O$. The sulphur of the zinc sulphide is oxidized to free sulphur and that of the sulphuric acid is reduced to sulphur dioxide. **HgS** is almost insoluble in HNO_3, dilute or concentrated, readily soluble in chlorine, nitrohydrochloric acid, or chloric acid if hot. Most other sulphides are soluble in hot HNO_3 (§**74,** 6*e*). Long continued boiling with water more or less completely decomposes the sulphides of **Ag**, **As**, **Sb**, **Sn**, **Fe**, **Co**, **Ni**, and **Mn**; no effect with sulphides of **Hg**, **Au**, **Pt**, **Mo**, **Cu**, **Cd**, and **Zn** (Clermont and Frommel, *A. Ch.*, 1879, (5), **18,** 203).

As a reagent, **hydrosulphuric acid,** gas or solution in water finds extended application in the analytical laboratory. The **grouping** of the **bases** for analysis depends very largely upon the relative solubilities of the sulphides. Hydrosulphuric acid in alkaline solution, *alkali sulphide* or *polysulphide,* is a scarcely less important reagent, being especially valuable in the subdivision of the metals of the **second group.**

The **sulphides** of the first four groups are insoluble. **Hydrosulphuric acid** transposes salts of the first two groups in acid, neutral, and alkaline mixtures, except arsenic, which is generally imperfectly precipitated unless some free acid or salt that is not alkaline to litmus be present. The result is a sulphide, but mercurosum forms mercuric sulphide and mercury, and arsenic acid may form arsenous sulphide and free sulphur. Ferric solutions are reduced to ferrous with liberation of sulphur. In acid mixture other third and fourth group salts are not disturbed, but from

solutions of their normal salts traces of cobalt, nickel, manganese, and zinc (§135, 6e) are precipitated.

Soluble sulphides transpose salts of the first four * groups. The result is a sulphide, except that with aluminum and chromium salts it is a hydroxide, hydrosulphuric acid being evolved. With mercurous salts, mercuric sulphide and mercury are formed; with ferric salts, ferrous sulphide and sulphur.

The precipitates have strongly marked **colors**—that of zinc being *white;* manganese, *flesh colored;* those of iron, copper, and lead, *black;* arsenic stannic and cadmium, *yellow;* antimony, *orange-red;* stannous, *brown;* mercury, successively white, yellow, orange, and *black.*

6. **Reactions.** *A.*—**With metals and their compounds.**—Some metals are converted into sulphides on being treated with hydrosulphuric acid; *e. g.*, **Ag**, **Cu**, **Hg**, etc. The alkali polysulphides slowly attack many metals with formation of sulphides: **Sn** becomes M'_2SnS_3; **Ag** becomes Ag_2S, no action with colorless $(NH_4)_2S$; **Ni** forms **NiS**; **Fe**, **FeS**; **Cu**, **CuS** and then Cu_2S (with colorless ammonium sulphide, $(NH_4)_2S$, Cu_2S is formed with evolution of hydrogen) (Priwozink, *A.*, 1872, **164**, 46).

The hydroxides or non-ignited oxides of **Pb″**, **Ag**, **Hg″**, **Sb**, **Sn**, **Bi‴**, **Cu**, **Cd**, **Fe″**, **Co″**, **Ni″**, **Mn″**, **Zn**, **Ba**, **Sr**, **Ca**, **Mg**, **K**, **Na**, and NH_4 unite with moist H_2S at ordinary temperature to form sulphides without change of the valence of the metal. In other cases the valence of the metal is changed, usually with liberation of sulphur.

1. Pb''^{+n} becomes **PbS** and **S**.

2. As^{V} in acid solution forms some As_2S_3 and **S**. See §69, 6c.

3. **Hg′** becomes **HgS** and **Hg**.

4. Cr^{VI} becomes **Cr‴** and **S**, if the H_2S be in excess: $2K_2Cr_2O_7 + 8H_2S = 4Cr(OH)_3 + 3S_2 + 2K_2S + 2H_2O$.

5. **Fe‴** becomes **Fe″** and **S**: $4FeCl_3 + 2H_2S = 4FeCl_2 + 4HCl + S_2$. If the solution be alkaline **FeS** is precipitated: $4FeCl_3 + 6K_2S = 4FeS + 12KCl + S_2$.

6. Co''^{+n} becomes **Co″** and **S**.

7. Ni''^{+n} becomes **Ni″** and **S**.

8. Mn''^{+n} becomes **Mn″** and **S**. In alkaline solution with excess of $KMnO_4$, an alkali sulphate is formed and MnO_2: $8KMnO_4 + 3K_2S = 3K_2SO_4 + 4K_2O + 8MnO_2$ (Schlagdenhafen, *Bl.*, 1874, (2), **22**, 16).

In the above reactions, if an alkaline sulphide be used instead of hydrosulphuric acid, the metal will be precipitated as a sulphide with the

*The normal fixed alkali sulphides (Na_2S, K_2S), precipitate solutions of calcium and magnesium salts as the hydroxides: $Ca(C_2H_3O_2)_2 + 2Na_2S + 2H_2O = Ca(OH)_2 + 2NaC_2H_3O_2 + 2NaHS$. No reaction with the acid fixed alkali sulphides (**NaHS**, **KHS**) or with ammonium sulphides (Pelouze, *A. Ch.*, 1866, (4), **7**, 172).

formation of an alkali hydroxide; except that the arsenic will remain in solution (§69, 5*c*) and the chromium will be precipitated as the hydroxide. Dry H_2S has no action on the dry salts of **Pb**, **Ag**, **Hg**, **As**, **Sb**, **Sn**, **Bi**, **Cu**, **Cd**, or **Co**; nor does it redden dry blue litmus (Hughes, *Phil. Mag.*, 1892, (5), **33**, 471).

Many insoluble sulphides, freshly precipitated, transpose the solutions of other metallic salts. In some cases the action is quite rapid at ordinary temperature, in others long-continued heating (several hours) at 100° is necessary. **PdS** is formed by action of $PdCl_2$ with sulphides of all the metals following in the series below named, but **PdS** is not transposed by solutions of the metals following. Silver salts form Ag_2S with sulphides of the metals following in the series but not with sulphides of **Pd** and **Hg**, etc.; **Pd**, **Hg**, **Ag**, **Cu**, **Bi**, **Cd**, **Sb**, **Sn**, **Pb**, **Zn**, **Ni**, **Co**, **Fe**, **As**, **Tl** and **Mn** (Schürmann, *A.*, 1888, **249**, 326).

B.—**With non-metals and their compounds.**

1. $H_3Fe(CN)_6$ becomes $H_4Fe(CN)_6$ and **S**. *Proof:* Boil to expel the excess of hydrosulphuric acid, then add ferric chloride (§126, 6*b*).

2. HNO_3 becomes **NO** and **S**. If the HNO_3 be hot and concentrated the sulphur is oxidized to sulphuric acid.

3. H_2S has no reducing action on the acids of phosphorus.

4. H_2SO_3 becomes pentathionic acid, $H_2S_5O_6$, and sulphur: $10H_2SO_3 + 10H_2S = 2H_2S_5O_6 + 5S_2 + 18H_2O$. With excess of H_2S the product is entirely free sulphur from both compounds: $2H_2SO_3 + 4H_2S = 3S_2 + 6H_2O$ (Debus, *J. C.*, 1888, **53**, 282).

H_2SO_4, dilute no action; concentrated and hot, **S** and SO_2 are formed: $2H_2SO_4 + 2H_2S = S_2 + 2SO_2 + 4H_2O$ (§256, 6*B4*).

5. **Cl** with H_2S in excess forms **HCl** and **S**; with **Cl** in excess forms **HCl** and H_2SO_4.

$HClO_3$ with H_2S in excess forms **HCl** and **S**; with $HClO_3$ in excess **HCl** and H_2SO_4.

6. **Br** with H_2S in excess forms **HBr** and **S**; with **Br** in excess **HBr** and H_2SO_4.

$HBrO_3$ with H_2S in excess forms **HBr** and **S**; with $HBrO_3$ in excess **HBr** and H_2SO_4.

7. **I** becomes **HI** and **S** (Filhol and Mellies, *A. Ch.*, 1871, (4), **22**, 58). HIO_3 becomes **HI** and **S**.

7. **Ignition.**—Dry hydrosulphuric acid gas is not decomposed when heated to 350° to 360°. At this temperature AsH_3 in presence of potassium polysulphide, K_2S_x, *liver of sulphur*, is decomposed: $2AsH_3 + 3K_2S_3 = 2K_3AsS_3 + 3H_2S$; thus furnishing a ready means of purifying H_2S for toxicological work (§69, 6*b*) (Pfordten, *B.*, 1884, **17**, 2897).

If air be excluded some sulphides may be sublimed unchanged; *e. g.*, **HgS**, As_2S_3, As_2S_5, Sb_2S_3, etc. In some cases part of the sulphur is separated, leaving a sulphide of a lower metallic valence: $2FeS_2 = 2FeS + S_2$. Some sulphides remain unchanged upon ignition in absence of air; *e. g.*, **FeS**, **MnS**, **CdS**, etc. All sulphides suffer some change on being ignited in the air; some slowly, others rapidly; Sb_2S_3, **CuS**, Al_2S_3, Cr_2S_3, etc., evolve SO_2 and leave

the oxide of the metal; HgS, Ag_2S, etc., evolve SO_2 and leave the free metal. All sulphides, as well as all other compounds of sulphur, when fused with KNO_3 or $KClO_3$ in presence of an alkali carbonate are oxidized to an alkali sulphate; forming NO or KCl and evolving CO_2. The metal is changed to the carbonate, oxide or the free metal (§228, 7).

When ignited on **charcoal with sodium carbonate**—or (*distinction from sulphates*) *if ignited in a porcelain crucible* with sodium carbonate—soluble *sodium sulphides* are obtained. The production of the sodium sulphide is proved by the *black stain* of Ag_2S, formed on metallic **silver** by a moistened portion of the fused mass. (Compounds of selenium and tellurium, §§112 and 113.)

8. **Detection.**—(*a*) The odor of the gas constitutes a delicate and characteristic test when not mixed with other gases having a strong odor. (*b*) The gas blackens filter paper moistened with a solution of lead acetate, delicate and characteristic. In the detection of traces of the gas, a slip of bibulous paper, so moistened, may be inserted into a slit in the smaller end of a cork, which is fitted to the test-tube, wherein the material to be tested is treated with sulphuric acid; the tube being set aside in a warm place for several hours. If any oxidizing agents are present—as chromates, ferric salts, manganic salts, chlorates, etc.—hydrosulphuric acid is not generated, but instead sulphur is separated, or sulphates are formed (6). (*c*) The gas blackens silver nitrate solution, delicate but PH_3, AsH_3, and SbH_3 also blacken silver nitrate solution. (*d*) By its reducing action upon nearly all oxidizing agents with separation of sulphur, which is detected according to §256, 8. $KMnO_4$ is perhaps the most delicate test but the least characteristic. (*e*) Its oxidation to a sulphate is characteristic in absence of other sulphur compounds. This method is usually employed with sulphides not transposed by dilute H_2SO_4; chlorine, nitrohydrochloric acid or bromine being the usual oxidizing agents. Also, these sulphides and certain supersulphides, attacked with difficulty by acids, as *iron pyrites* and *copper pyrites*, are reduced and dissolved, with evolution of *hydrosulphuric acid*, by **dilute sulphuric acid with zinc.** The gas, with its excess of hydrogen, may be tested by method (*f*). (*f*) Sodium nitroferricyanide $Na_2[Fe(CN)_5(NO)].2H_2O$ also known as sodium nitroprusside gives a very delicate and characteristic test for H_2S as an alkali sulphide. The gas is passed into ammonium hydroxide; and to this mixture a 20 per cent solution of the reagent is added, producing a transient reddish-purple color. Free H_2S, dilute, remains colorless; a concentrated solution gives a blue color, due to the reducing action of the H_2S on the ferricyanide. Caustic alkali hinders the reaction. 0.000018 gram of H_2S, as gas or alkali sulphide, can be detected by this reagent (Reichard, *Z.*, **43**, 222). (*g*) The most delicate test for hydrogen sulphide involves the formation of methylene blue (E. Fisher, *Ber.*, **16**, 2234). By this test 0.02 mg. of hydrogen sulphide in a liter will give a blue color after standing half an hour. The test is carried out as follows: to the solution to be tested is added one-tenth of its volume

of concentrated **HCl**, then a small amount of dimethylparaphenylendiamine sulphate ($NH_2.C_6H_4.N(CH_3)_2.H_2SO_4$) and after it has dissolved a drop or two of dilute ferric chloride solution.

For method of separation of the various sulphur compounds from each other consult Kynaston (*J. C.*, 1859, **11**, 166), Bloxam (*C. N.*, 1895, **72**, 63), Votoček (Ber., 1907, **40**, 414) and Autenrieth and Windaus (*Z.*, 1898, 295).

9. **Estimation.**—Sulphides are usually oxidized to H_2SO_4 (by chlorine, bromine, or nitrohydrochloric acid, or by fusion with KNO_3 and Na_2CO_3) precipitated with $BaCl_2$ and weighed as $BaSO_4$.

§258. Thiosulphuric acid. $H_2S_2O_3 = 114.136$.

Dithionous acid.

$$H'_2(S_2)^{IV}O^{-''}_3,\ H-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-S-H.*$$

1. **Properties.**—Thiosulphuric acid, $H_2S_2O_3$ (formerly called hyposulphurous acid), has not been isolated; but it almost certainly exists in dilute solutions, when a dilute weak acid is added to a solution of sodium thiosulphate, $Na_2S_2O_3$, soon beginning to decompose into H_2SO_3 and **S** (Landolt, *B.*, 1883, **16**, 2985). The thiosulphates are not particularly stable compounds, some decomposing almost immediately upon forming; *e. g.*, mercury thiosulphates. Alkali thiosulphates decompose upon heating into sulphate and polysulphide: $4Na_2S_2O_3 = 3Na_2SO_4 + Na_2S_5$. Other salts give also **S** and H_2S. Boiling solution of a thiosulphate gives a sulphate and H_2S or a sulphide of the metal.

2. **Occurrence.**—Not found in nature.

3. **Formation.**—Thiosulphates are formed by the oxidation of alkali or alkaline earth polysulphides by exposure to the air or by SO_2 or $K_2Cr_2O_7$: $2CaS_5 + 3O_2 = 2CaS_2O_3 + 3S_2$; $4Na_2S_5 + 6SO_2 = 4Na_2S_2O_3 + 9S_2$; $2K_2S_5 + 4K_2Cr_2O_7 + 13H_2O = 5K_2S_2O_3 + 8Cr(OH)_3 + 2KOH$ (Doepping, *A.*, 1843, **46**, 172; Gueront, *C. r.*, 1872, **75**, 1276). Also by heating ammonium sulphate with phosphorus pentasulphide (Spring, *B.*, 1874, **7**, 1157).

4. **Preparation.**—Thiosulphates are prepared by boiling sulphur in a solution of normal alkali sulphite: $2Na_2SO_3 + S_2 = 2Na_2S_2O_3$. Fixed alkali or alkaline earth hydroxides with sulphur also form thiosulphates: $3Ca(OH)_2 + 6S_2 = 2CaS_5 + CaS_2O_3 + 3H_2O$ (Filhol and Senderens, *C. r.*, 1883, **96**, 839; Senderens, *C. r.*, 1887, **104**, 58). *Commercial* sodium thiosulphate is prepared by passing SO_2 into "soda waste" suspended in water, calcium thiosulphate being formed. This is treated with sodium sulphate, filtered and evaporated to crystallization.

5. **Solubilities.**—The larger number of the thiosulphates are **soluble in water**; those of barium, lead and silver being only very sparingly soluble. The thiosulphates are insoluble in alcohol. They are decomposed, but not fully dissolved, by acids, the decomposition leaving a residue of sulphur.

* Bunte, *B.*, 1874, **7**, 646.

Alkali thiosulphate solutions dissolve the thiosulphates of lead and silver; also the chloride, bromide and iodide of silver, and mercurous chloride: the iodide and sulphate of lead; the sulphate of calcium, and some other precipitates—by formation of soluble *double thiosulphates*:

$$Ag_2S_2O_3 + Na_2S_2O_3 = 2NaAgS_2O_3$$
$$AgCl + Na_2S_2O_3 = NaAgS_2O_3 + NaCl$$
$$PbSO_4 + 3Na_2S_2O_3 = Na_4Pb(S_2O_3)_3 + Na_2SO_4$$

6. **Reactions.**—*A.*—**With metals and their compounds.**—With soluble thiosulphates, solutions of **lead** and **silver salts** are precipitated as thiosulphates, white, soluble in excess of alkali thiosulphate. These precipitates decompose upon standing, rapidly on warming, into sulphides and sulphuric acid: $Ag_2S_2O_3 + H_2O = Ag_2S + H_2SO_4$. Soluble **mercury salts** with sodium thiosulphate form a white precipitate, almost instantly turning black with decomposition to mercuric sulphide. $Na_2S_2O_3$ blackens $HgCl$, a portion of the mercury going into solution, colorless, reprecipitated black upon warming.

Acid solutions of **arsenic** and **antimony** are precipitated by hot solution of $Na_2S_2O_3$ as sulphides, As_2S_3 and Sb_2S_3 (a separation from tin,* which is not precipitated) (6*e*, §§69, 70 and 71). Solutions of **copper salts** with thiosulphates, on long standing, precipitate cuprous salt, changed by boiling to cuprous sulphide and sulphuric acid (separation from cadmium, §78, 6*c*).

Solutions of **ferric salts** are reduced to ferrous salts with formation of sodium tetrathionate: $2FeCl_3 + 2Na_2S_2O_3 = 2FeCl_2 + 2NaCl + Na_2S_4O_6$; used as a quantitative method of estimation, with a few drops of potassium thiocyanate as an indicator. **Chromic acid** (chromates in acid solution) are reduced to chromic salts with oxidation of the thiosulphate.

Permanganates in neutral solution become manganese dioxide, in acid solution the reduction is complete to manganous salt, a sulphate and dithionate being formed (Luckow, *Z.*, 1893, **32**, 53).

Barium chloride forms a white precipitate of barium thiosulphate, BaS_2O_3, nearly insoluble in water; 100 parts of water dissolve 0.2675 part of $BaS_2O_3 \cdot H_2O$ at 17.5°. **Calcium chloride** forms no precipitate (distinction from a sulphite).

B.—**With non-metals and their compounds.**—When thiosulphates are decomposed by acids, the constituents of thiosulphuric acid are dissociated as sulphurous acid and sulphur. Nearly all acids in this way decompose thiosulphates: $2Na_2S_2O_3 + 4HCl = 4NaCl + 2H_2SO_3 + S_2$.

Thiosulphates are reducing agents—even stronger and more active than the sulphites to which they are so easily converted. This reduction is illustrated by the action on arsenic compounds, on ferric salts and on chromates and permanganates as given above. Also the halogens are reduced to the halide salts forming a tetrathionate: $2Na_2S_2O_3 + I_2 = 2NaI + Na_2S_4O_6$. If chlorine or bromine be in excess the tetrathionate is further oxidized to a sulphate: $Na_2S_2O_3 + 4Cl_2 + 5H_2O = Na_2SO_4 + H_2SO_4 + 8HCl$. Chloric, bromic and iodic acids are first reduced to the corresponding halogens and then with an excess of the thiosulphate to the halides, always accompanied with the separation of sulphur. Nitric acid is reduced to nitric oxide with the separation of sulphur.

7. **Ignition.**—**On ignition**, or by heat short of ignition, all thiosulphates are decomposed. Those of the alkali metals leave sulphates and polysulphides (*a*), others yield sulphurous acid with sulphides, or sulphates, or both. The capacity of thiosulphates for rapid oxidation, renders their mixture with chlorates, nitrates, etc., *explosive*, in the dry way. **Chlorates** with thiosulphates explode violently in the mortar. **Cyanides** and ferricyanides, fused with thiosulphates, form thiocyanates, which may be dissolved by alcohol from other products. By fusion on charcoal with Na_2CO_3, thiosulphates form sulphides (*b*) and (*c*); and by fusion with an alkali carbonate and nitrate or chlorate,

* According to Vortmann (*M.*, 1886, 7, 418) sodium thiosulphate may be used instead of hydrosulphuric acid in the second group of bases. An excess of the reagent is to be avoided and nitric acid should be absent.

a sulphate is formed (*d*). By ignition of a metallic salt with $Na_2S_2O_3$ in a dry test-tube the characteristic colored sulphide of the metal is obtained (Landauer, *B.*, 1872, **5**, 406).

(*a*) $4Na_2S_2O_3 = Na_2S_5 + 3Na_2SO_4$

(*b*) $Na_2S_2O_3 + Na_2CO_3 + 2C = 2Na_2S + 3CO_2$

(*c*) $2PbS_2O_3 + 4Na_2CO_3 + 5C = 4Na_2S + 2Pb + 9CO_2$

(*d*) $3Na_2S_2O_3 + 3Na_2CO_3 + 4KClO_3 = 6Na_2SO_4 + 4KCl + 3CO_2$

8. **Detection.**—In **analysis**, thiosulphates are distinguished by giving a precipitate of sulphur with evolution of sulphurous anhydride when their solutions are treated with hydrochloric acid; by their intense reducing power, shown in the blackening of the silver precipitate; and by non-precipitation of calcium salts.

The *precipitation of sulphur with evolution of sulphurous anhydride*, by addition of **dilute acids**—as **hydrochloric** or acetic—is characteristic of thiosulphates. It will be understood, however, that in presence of oxidizing agents, which can be brought into action by the acid, sulphides will likewise give a precipitate of **sulphur.**

In the presence of a sulphate and sulphite the thiosulphate is detected as follows: Add $BaCl_2$ and NH_4Cl in excess, then **HCl** to solution of all but the $BaSO_3$. Filter and treat the filtrate with iodine, forming $BaSO_4$ of the sulphite and BaS_4O_6 of the thiosulphate. Filter and add bromine to the filtrate, which then forms $BaSO_4$ (Smith, *C. N.*, 1895, **72**, 39).

Sulphides, sulphites and thiosulphates may be separated as follows:—Add to the neutral solution cadmium carbonate, shake and filter off the cadmium sulphide and excess of cadmium carbonate. Test the filtrate for sulphide with sodium nitroprusside and again add cadmium carbonate until the sulphide is entirely removed. Add strontium nitrate to the filtrate, allow to stand overnight and filter off the strontium sulphite. Test the precipitate for sulphurous acid. Test the filtrate for thiosulphuric acid by acidifying with **HCl** and warming. (Autenrieth and Windaus, *Z.*, 1898, 295.)

9. **Estimation.**—By titration with a standard solution of iodine, or by titrating the iodine liberated by a standard solution of potassium dichromate (§§**125**, 10, and **279**, 6*B*7).

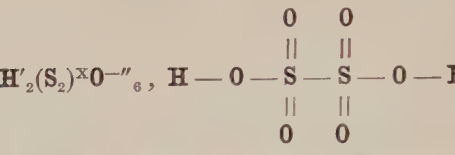
§259. Hyposulphurous acid. $H_2SO_2 = 66.076$.

(*Hydrosulphurous or dithionous acid.*)

$$H'_2S''O^{-''}{}_2,\ H-O-S-H$$
$$\|$$
$$O$$

Obtained by Schützenberger (*C. r.*, 1869, **69**, 196) by the action of zinc on sulphurous acid: $Zn + 2SO_2 + H_2O = ZnSO_3 + H_2SO_2$. The sodium salt is formed by treating a concentrated solution of sodium acid sulphite with zinc filings: $Zn + 3NaHSO_3 = ZnSO_3 + Na_2SO_3 + NaHSO_2 + H_2O$. In the formation of the free acid or of the sodium salt no hydrogen is evolved. It is a very unstable compound, a strong reducing agent, rapidly absorbs oxygen from the air, becoming sulphurous acid or a sulphite. According to Bernthsen (*B.*, 1881, **14**, 438) the sodium salt does not contain hydrogen. He gives the formula as $Na_2S_2O_4$: $Zn + 4NaHSO_3 = ZnSO_3 + Na_2SO_3 + Na_2S_2O_4 + 2H_2O$. It is used in the preparing of indigo white for the printing of cotton fabrics. See also Dupré, *J. C.*, 1867, **20**, 291.

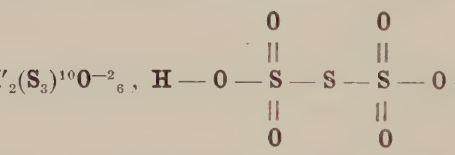
§260. Dithionic acid. $H_2S_2O_6 = 162.136$.



Known only in the form of its salts and as a solution of the acid in water. The free acid or the anhydride has not been prepared. The manganous salt is prepared by the action of a solution of sulphurous acid upon manganese dioxide at a low temperature: $MnO_2 + 2H_2SO_3 = MnS_2O_6 + 2H_2O$. Similar results are obtained with nickelic or ferric oxides (Spring and Bourgeois, *Bl.*, 1886, **46**, 151). The acid is obtained by treating the manganous salt with $Ba(OH)_2$ and the filtrate from this with the calculated amount of H_2SO_4. It is a colorless solution and may be evaporated in a vacuum until it has a specific gravity of 1.347. It decomposes upon further heating: $H_2S_2O_6 = H_2SO_4 + SO_2$. *All other thionic compounds decompose upon heating with separation of sulphur.* By exposure to the air dithionic acid is oxidized to sulphuric acid. All dithionates are soluble in water and may be purified by evaporation and crystallization (Gelis, *A. Ch.*, 1862, (3), **65**, 230).

Dithionic acid is also prepared by carefully adding a potassium iodide solution of iodine to sodium acid sulphite (Holst and Otto, *Arch. Pharm.*, 1891, **229**, 171); Spring and Bourgeois (*Arch. Pharm.*, 1891, **229**, 707) contradict the above statement.

§261. Trithionic acid. $H_2S_3O_6 = 194.196$.



The free acid and anhydride are not known. The potassium salt is prepared by boiling potassium acid-sulphite with sulphur (*a*); by treating potassium thiosulphate with sulphurous acid (*b*) (no action with sodium thiosulphate) (Baker, *C. N.*, 1877, **36**, 203; Villiers, *C. r.*, 1889, **108**, 402); by the action of iodine on a mixture of sodium sulphite and thiosulphate (*c*) (Spring, *B.*, 1874, **7**, 1157):

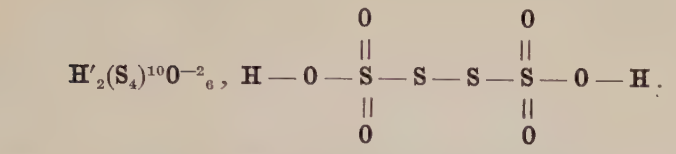
(*a*) $12KHSO_3 + S_2 = 4K_2S_3O_6 + 2K_2SO_3 + 6H_2O$

(*b*) $4K_2S_2O_3 + 6SO_2 = 4K_2S_3O_6 + S_2$

(*c*) $Na_2SO_3 + Na_2S_2O_3 + I_2 = Na_2S_3O_6 + 2NaI$

The acid is prepared by adding perchloric or fluosilicic acid to the potassium salt. The acid is quite unstable; at low temperature in a vacuum it decomposes into SO_2, S and H_2SO_4. The salts are quite stable; they are not oxidized by chloric or iodic acids, while the free acid is rapidly oxidized by these acids. Fixed alkalis or sodium amalgam change the trithionate to sulphite and thiosulphate (Spring, *l. c.*).

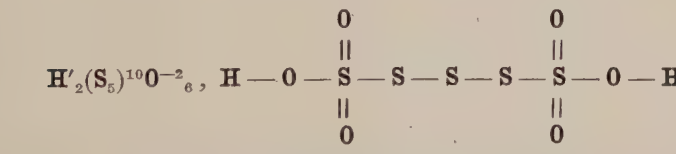
§262. Tetrathionic acid. $H_2S_4O_6 = 226.256$.



The salts are soluble in water and are comparatively stable. They are best obtained in crystalline form by adding alcohol to their solutions in water. The acid has not been isolated but it is much more stable than the tri or pentathionic acids. In dilute solution it can be boiled without decomposition. The concentrated solution decomposes into H_2SO_4, SO_2 and S.

Tetrathionates are prepared by adding iodine to the thiosulphates: $2BaS_2O_3 + I_2 = BaS_4O_6 + BaI_2$ (Maumené, *C. r.*, 1879, **89**, 422). The lead salt is obtained by the oxidation of lead thiosulphate by lead peroxide in presence of sulphuric acid: $2PbS_2O_3 + PbO_2 + 2H_2SO_4 = PbS_4O_6 + 2PbSO_4 + 2H_2O$ (Chancel and Diacon, *J. pr.*, 1863, **90**, 55). To obtain the acid the lead should be removed by the necessary amount of sulphuric acid, and not by hydrosulphuric acid, which causes the formation of some pentathionic acid. A number of other oxidizing agents may be used to form the tetrathionate from the thiosulphate (Fordos and Gelis, *C. r.*, 1842, **15**, 920). Sodium amalgam reconverts the tetrathionate into the thiosulphate: $Na_2S_4O_6 + 2Na = 2Na_2S_2O_3$ (Lewes, *J. C.*, 1880, **39**, 68; 1881, **41**, 300). Tetrathionic acid is also formed with pentathionic acid in the reactions between solutions of H_2S and SO_2 (Wackenroder's solution, *A.*, 1846, **60**, 189). See also Curtius and Henkel (*J. pr.*, 1888, (2), **37**, 137). The acid gives no precipitate of sulphur when treated with potassium hydroxide (distinction from pentathionic acid).

§263. Pentathionic acid. $H_2S_5O_6 = 258.316$.



Only known in the salts and in the solution of the acid in water. It is formed by the action of H_2S upon SO_2 in the presence of water (*a*); by the action of water on sulphur chloride (*b*); by the decomposition of lead thiosulphate with H_2S (Persoz, *Pogg.*, 1865, 124, 257):

a. $10H_2SO_3 + 10H_2S = 2H_2S_5O_6 + 5S_2 + 18H_2O$

b. $10S_2Cl_2 + 12H_2O = 2H_2S_5O_6 + 5S_2 + 20HCl$

The filtrate from the decomposition of SO_2 by H_2S is known as Wackenroder's solution (*Arch. Pharm.*, 1826, **48**, 140). It has been shown to contain the tri and tetrathionic acids in addition to the pentathionic acid (Debus, *C. N.*, 1888, **57**, 87). Pentathionic acid may be concentrated in a vacuum until it has a specific gravity of 1.6; farther concentration or boiling heat alone decomposes it into H_2SO_4, SO_2 and S. The solution of the acid does not bleach indigo. When treated with a fixed alkali hydroxide an immediate precipitate of sulphur is obtained (distinction from $H_2S_4O_6$): $4H_2S_5O_6 + 20NaOH = 6Na_2SO_3 + 4Na_2S_2O_3 + 3S_2 + 14H_2O$ (Takamatsu and Smith, *J. C.*, 1880, **37**, 592); or if the $NaOH$ be added short of neutralization: $10H_2S_5O_6 + 20NaOH = 10Na_2S_4O_6 + 5S_2 + 20H_2O$. Neutralization of pentathionic acid with barium carbonate gives barium tetrathionate and sulphur (Takamatsu and Smith, *J. C.*, 1882, **41**, 162; Lewes, *J. C.*, 1881, **39**, 68). See also Spring, *A.*, 1879, **199**, 97.

§264. *Reactions to distinguish Tetra- and Pentathionic Acids from each other, and from the other Thionic Acids.**

Reagents.	Dithionic acid, $H_2S_2O_6$.	Trithionic acid, $H_2S_3O_6$.	Tetrathionic acid, $H_2S_4O_6$.	Pentathionic acid, $H_2S_5O_6$.
Potassium hydroxide	No precipitate	No precipitate	No precipitate	Immediate precipitate of sulphur, redissolving gradually on standing, if not in much excess and coagulated.
Dilute hydrochloric acid.	No action	Evolution of SO_2, and precipitate of **S**.	No action	No action.
Mercurous nitrate	No precipitate	Immediate black precipitate, becoming white on standing.	Yellow precipitate, gradually darkening.	At first yellow precipitate, turning white with excess of reagent on standing.
Silver nitrate	No precipitate	Yellow precipitate, soon becoming black.	Yellow precipitate, soon turning black, and also on adding ammonium hydroxide.	Yellow precipitate, gradually darkening; black on adding ammonium hydroxide.
Ammoniacal silver nitrate.		No brown coloration, even on standing. On warming, Ag_2S formed.	No dark or brown coloration, even on standing, *unless warmed.*	Almost immediate brown coloration, becoming black on warming.
Mercuric cyanide	No precipitate		At first yellow precipitate; turns black on warming, with evolution of **HCN.**	At first yellow precipitate, gradually turning black on heating, with evolution of **HCN.**
Mercuric chloride	No precipitate	Yellow precipitate, becoming white with excess of reagent.	On warming, white precipitate.	On warming, whitish yellow precipitate.
Potassium acid-sulphide solution (**KHS**).			White precipitate of sulphur	White precipitate of sulphur.
Dilute solution of potassium permanganate.	One drop, immediate brown precipitate.	One drop, immediate brown precipitate, even in presence of dilute H_2SO_4.	Decolorized, without addition of dilute H_2SO_4.	Decolorized, without addition of dilute of H_2SO_4.

* Takamatsu and Smith, *J. C.*, 1880, **37**, 608.

§265. Sulphurous anhydride. $SO_2 = 64.06$.

Sulphurous acid. $H_2SO_3 = 82.076$.

$$S^{IV}O^{-''}_2 \text{ and } H'_2S^{IV}O^{-''}_3, \quad O=S=O \text{ and } H-O-\overset{O}{\overset{\|}{S}}-O-H.$$

1. **Properties.**—Sulphurous anhydride, SO_2, sulphur dioxide, is a colorless gas of a strong suffocating odor of burning sulphur. *Specific gravity* of the liquid at 0°, 1.4338 (Cailletet and Matthias, *C. r.*, 1887, **104**, 1563); of the gas at 0° and 760 mm. pressure, 2.2369 (Leduc, *C. r.*, 1893, **117**, 219). It is liquefied at atmospheric pressure upon cooling to —10° (Pierre, *C. r.*, 1873, **76**, 214). In an open dish it evaporates rapidly, the temperature of the remaining liquid dropping to —75°; or by evaporating rapidly under diminished pressure it becomes a white wooly solid. Cooled to —76.1° it becomes a snow-white solid (Faraday, *C. r.*, 1861, **53**, 846). The dry gas is not combustible in the air, does not react acid to litmus, but in presence of water it has a *marked acid reaction.* The gas and the free acid, not the salts, are quite poisonous, due to the absorption of the SO_2 by the blood and oxidation to H_2SO_4. The gas is soluble in water, forming probably sulphurous acid, H_2SO_3. The pure acid has not been isolated, but forms salts mono and dibasic as if derived from such an acid (Michaelis and Wagner, *B.*, 1874, **7**, 1073). It has a strong odor from vaporization of sulphurous anhydride, which is soon completely expelled upon boiling. The acid oxidizes slowly in the air, forming H_2SO_4, hence sulphurous acid usually gives reactions for sulphuric acid. Light seems to play an important part in this oxidation (Loew, *Am. S.*, 1870, **99**, 368). The moist gas or a solution of the acid is a strong bleaching agent, however not acting alike in all cases. Wool, silk, feathers, sponge, etc., are permanently bleached; also many vegetable substances, straw, wood, etc.; yellow colors and chlorophyll are not bleached; red roses are temporarily bleached, immersion in dilute H_2SO_4 restoring the color.

2. **Occurrence.**—Found free in volcanic gases (Ricciardi, *B.*, 1887, **20**, 464).

3. **Formation.**—(*a*) By burning sulphur in air. (*b*) By heating sulphur with various metallic oxides. (*c*) By decomposition of thiosulphates with HCl. (*d*) By burning H_2S or CS_2 in air. (*e*) By the action of hot concentrated sulphuric acid on metals, carbon, sulphur, etc. (*f*) By heating sulphur with sulphates. (*g*) By decomposition of sulphites with acids:

(*a*) $S_2 + 2O_2 = 2SO_2$

(*b*) $MnO_2 + S_2 = MnS + SO_2$

$2Pb_3O_4 + 5S_2 = 6PbS + 4SO_2$

(*c*) $2Na_2S_2O_3 + 4HCl = 4NaCl + 2SO_2 + S_2 + 2H_2O$

(*d*) $2H_2S + 3O_2 = 2SO_2 + 2H_2O$

$CS_2 + 3O_2 = 2SO_2 + CO_2$

(*e*) $Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O$

$S_2 + 4H_2SO_4 = 6SO_2 + 4H_2O$

$C + 2H_2SO_4 = 2SO_2 + CO_2 + 2H_2O$

(*f*) $FeSO_4 + S_2 = FeS + 2SO_2$

(*g*) $Na_2SO_3 + 2H_2SO_4 = 2NaHSO_4 + SO_2 + H_2O$

4. **Preparation.**—(*a*) By heating moderately concentrated sulphuric acid with copper turnings: $Cu + 2H_2SO_4 = CuSO_4 + SO_2 + 2H_2O$. The gas is dried by passing through concentrated sulphuric acid. (*b*) By heating a mixture of sulphur and cupric oxide in a hard glass tube. (*c*) In a Kipp's generator by decomposing cubes composed of three parts calcium sulphite and one part of calcium sulphate, with dilute sulphuric acid (Neumann, *B.*, 1887, **20**, 1584).

Preparation of sulphites.—The sulphites of the ordinary metals are usually made by action of sulphurous acid upon the oxides or hydroxides of the metals. They are normal, except mercurous, which is acid, and chromium, aluminum

and copper, which are basic. Sulphurous acid precipitates solutions of metals of the first and second groups, except copper and cadmium.

The sulphites of the alkalis precipitate solutions of the other metals except chromium salts; and some normal sulphites may be made in this manner. The sulphites of silver, mercury, copper and ferricum (known only in solution) are unstable, the sulphurous acid becoming sulphuric at the expense of the base, which is reduced to a form having a less number of bonds. With the unstable stannous sulphite the action is the reverse. (See 6*A*.) All sulphites by exposure to the air slowly absorb oxygen, and are partially converted into sulphates.

5. **Solubilities.**—One volume of water at 0° dissolves 68.861 volumes of sulphurous anhydride; at 20°, 36.206 volumes (Carius, *A.*, 1855, **94,** 148); or at 20°, 0.104 part by weight (Sims *J. C.*, 1862, **14,** 1). One volume of alcohol dissolves at 15°, 116 vol. SO_2. Charcoal absorbs 165 volumes, camphor 308 volumes, glacial acetic acid 318 volumes of the gas. Liquid sulphurous anhydride dissolves **P**, **S**, **I**, **Br** and many gases.

The sulphites of the metals of the alkalis are freely soluble in water; the normal sulphites of all other metals are insoluble, or but very slightly soluble in water. The sulphites of the metals of the alkaline earths, and some others, are soluble in solution of sulphurous acid, the solution being precipitated on boiling. The alkali bases form acid sulphites (bisulphites), which can be obtained in the solid state, but evolve sulphurous anhydride. The sulphites are insoluble in alcohol. They are decomposed by all acids except carbonic and boric, and in some instances, hydrosulphuric.

6. **Reactions.** *A.*—**With metals and their compounds.**—Sulphurous acid reacts with **Zn**, **Fe**, **Sn**, and **Cu** to form hyposulphurous acid, H_2SO_2 (Schützenberger, *C. r.*, 1869, **69,** 196). With **Zn** in the presence of **HCl** it is reduced to hydrosulphuric acid: $3Zn + 6HCl + H_2SO_3 = 3ZnCl_2 + H_2S + 3H_2O$. Free sulphurous acid precipitates solutions of first and second group metals except those of copper and cadmium; solutions of other metallic salts are not precipitated owing to the solubility of the sulphites in acids.

Alkali sulphites precipitate solutions of all other metallic salts. The precipitates, mostly white, are soluble in acetic acid. The precipitates of **Pb**, **Hg**, **Ba**, **Sr**, and **Ca** are usually accompanied by sulphates, due to the fact that soluble sulphites nearly always contain sulphates (4).

Solution of **lead acetate** precipitates, from solutions of sulphites, *lead sulphite*, $PbSO_3$, white, easily soluble in dilute nitric acid; and not blackening when boiled (distinction from thiosulphate). Solution of **silver nitrate** gives a white precipitate of *silver sulphite*, Ag_2SO_3, easily soluble in very dilute nitric acid or in excess of alkaline sulphite, and turning dark-brown when boiled, by formation of metallic silver and sulphuric acid. Solution of mercurous nitrate with sodium sulphite gives a gray precipitate of metallic mercury. Solution of **mercuric chloride** produces no change in the cold; but on boiling, the white *mercurous chloride* is precipitated, with formation of sulphuric acid. Still further digestion, with sufficient sulphite, reduces the white mercurous chloride to gray metallic mercury (§**58,** 6*e*).

Solution of **ferric chloride** gives a *red solution of ferric sulphite*, $Fe_2(SO_3)_3$; or, in more concentrated solutions, a *yellowish precipitate* of

basic ferric sulphite, also formed by addition of alcohol to the red solution. The red solution is decolored on boiling; the acid radical reducing the basic radical, and forming ferrous sulphate.

Solution of **barium chloride** gives a white precipitate of *barium sulphite*, $BaSO_3$, easily soluble in dilute hydrochloric acid—*distinction from sulphate*, which is undissolved, and should be filtered out. Now, on adding to the filtrate **nitrohydrochloric acid**, a precipitate of barium sulphate is obtained—evidence that sulphite has been dissolved by the hydrochloric acid:

$$BaSO_3 + 2HCl = BaCl_2 + H_2SO_3$$
$$BaCl_2 + H_2SO_3 + Cl_2 + H_2O = BaSO_4 + 4HCl$$

One part of barium sulphite is dissolved by 46,000 parts of water at 18°.

Calcium chloride reacts similar to barium chloride, the precipitate of calcium sulphite being *less* soluble in water than the corresponding sulphate. One part of calcium sulphite is dissolved by 800 parts of water at 18° while one part of the strontium salt is dissolved by 30,000 parts water at 18°.

Sulphurous acid and **sulphites** are active **reducing agents** by virtue of their **capacity for oxidation to sulphuric acid and sulphates.**

The reactions with silver, mercury and ferricum given above illustrate the reducing action, and the following should also be noted:

PbO_2 becomes lead sulphate.

As^V forms arsenous and sulphuric acids.

Sb^V forms Sb'''.

Cu'' becomes cuprous sulphate.

Cr^{VI} forms chromic sulphate.

Co''' forms cobaltous sulphate.

Ni''' forms nickel sulphate.

Mn''^{+n} forms manganous sulphate.

With MnO_2 in the cold, manganous dithionate, MnS_2O_6, is formed (*Gmelin's Hand-book*, **2**, 174).

With *stannous chloride* sulphurous acid acts as an **oxidizing agent**, forming stannic sulphide and stannic chloride or stannic chloride and hydrosulphuric acid, according to the amount of hydrochloric acid present (§71, 6*e*).

B.—**With non-metals and their compounds.**—Upon other acids sulphurous acid acts as a reducing agent, except with hypophosphorous, phosphorous, and hydrosulphuric acids.

1. $H_3Fe(CN)_6$ forms $H_4Fe(CN)_6$ and H_2SO_4.

2. HNO_2 and HNO_3 form NO and H_2SO_4.

3. $PH_3 + 2H_2SO_3 = H_3PO_4 + S_2 + 2H_2O$ (Carvazzi, *Gazzetta*, 1886, **16**, 169). H_3PO_2 becomes H_3PO_4 and the SO_2 is reduced to **S**, and with excess of H_3PO_2 to H_2S. H_3PO_3 forms H_3PO_4 and H_2S (§253, 6).

4. H_2S forms **S** from both compounds: $4H_2S + 2SO_2 = 3S_2 + 4H_2O$. See also §263.

5. **Cl**, $HClO$, and $HClO_3$ form hydrochloric and sulphuric acids.

6. **Br** forms hydrobromic and sulphuric acids. $HBrO_3$ forms first bromine then hydrobromic acid, sulphuric acid in both cases.

7. **I** forms hydriodic and sulphuric acids. In presence of hydrochloric acid and a barium salt it serves as a means of detecting a sulphite mixed with a sulphate and a thiosulphate (Smith, *C. N.*, 1895, **72**, 39). HIO_3 forms first iodine then hydriodic acid, sulphuric acid in both cases.

7. **Ignition.**—Acid sulphites heated in sealed tube to 150° are decomposed into sulphates and sulphur (Barbaglia and Gucci, *B.*, 1880, **13**, 2325; Berthelot, *A. Ch.*, 1864, (4), **1**, 392). Dry SO_2 at high heat with many metals is decomposed, forming a sulphide and sulphate or sulphite (Uhl, *B.*, 1890, **23**, 2151). Sulphites are decomposed by heat into oxides and sulphurous anhydride: $CaSO_3 = CaO + SO_2$; or into sulphates and sulphides: $4Na_2SO_3 = 3Na_2SO_4 + Na_2S$.

8. **Detection.**—Free *sulphurous acid* is detected by its odor and by its decolorizing action upon a solution of $KMnO_4$ or **I** (Hilger, *J. C.*, 1876, **29**, 443). The reaction with iodic acid is also employed as a test for sulphurous acid (as well as for iodic). A mixture of **iodic acid and starch** is turned violet to blue by traces of sulphurous acid or sulphites in vapor or in solution, the color being destroyed by excess of the sulphurous acid or the sulphite. *Sulphites* are distinguished from *sulphates* by failure to precipitate with $BaCl_2$ in presence of HCl. After removal of the $BaSO_4$ by filtration the sulphite is oxidized to sulphate by chlorine water and precipitated by the excess of $BaCl_2$ present. For separation from sulphides and thiosulphates see §258, 8.

Normal potassium sulphite, K_2SO_3, is alkaline to litmus but when treated with $BaCl_2$ gives a neutral solution. The acid sulphite, $KHSO_3$, is neutral to litmus but with $BaCl_2$ gives an acid solution: $2KHSO_3 + BaCl_2 = BaSO_3 + 2KCl + SO_2 + H_2O$ (Villiers, *C. r.*, 1887, **104**, 1177).

9. **Estimation.**—(*a*) After converting into H_2SO_4 by HNO_3 or **Cl** it is precipitated by $BaCl_2$ and weighed as $BaSO_4$. (*b*) The oxidation is effected by fusing with Na_2CO_3 and KNO_3 (equal parts). (*c*) A standard solution of iodine is added, and the excess of iodine determined by a standard solution of $Na_2S_2O_3$.

§266. Sulphuric acid. $H_6SO_4 = 98.076$.

$$H'_2S^{VI}O^{-''}_4, H-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-H.$$

1. **Properties.**—Absolute sulphuric acid, H_2SO_4, is a colorless oily liquid (oil of vitriol); specific gravity, 1.8371 at 15° (Mendelejeff, *B.*, 1884, **17**, 2541). According to Marignac (*A. Ch.*, 1853, (3), **39**, 184), it begins to boil at about 290°, ascending to 338° with partial decomposition. At temperatures much below the boiling point (160°) it vaporizes from open vessels, giving off heavy, white, suffocating vapors, exciting coughing without giving premonition by odor. At ordinary temperature it is non-volatile and inodorous. At low temperatures it solidifies to a crystalline mass. The freezing point is greatly influenced by the amount of water present. When the acid contains one molecule of water, $H_2SO_4.H_2O$, the melting point is highest, +7.5° (Pierre and Puchot, *A. Ch.*, 1874, (5), 164).

H_2SO_4 is a very strong acid and, because of its high boiling point, displaces all the volatile inorganic acids; on the other hand it is displaced, when heated above its boiling point, by phosphoric, boric, and silicic acids. It is a dibasic acid, forming two series of salts, $M'HSO_4$ and M'_2SO_4. It is miscible with **water** in all proportions with production of heat; it abstracts water from the air (use in desiccators), and quickly abstracts the elements of water from many **organic compounds**, and leaves their *carbon*, a characteristic charring effect. It dissolves in alcohol, without decomposing it —but if in sufficient proportion producing ethylsulphuric acid, $HC_2H_5SO_4$.

Sulphuric anhydride, SO_3, is a colorless, fibrous or waxy solid, melting at 14.8° (Rebs, *A.*, 1888, **246**, 379), boiling at 46° (Schulz-Sellak, *B.*, 1870, **3**, 215), and vaporizing with heavy white fumes in the air at ordinary temperatures. It is very deliquescent, and on contact with water combines rapidly, forming sulphuric acid with generation of much heat.

2. **Occurrence.**—Found free in the spring water of volcanic districts. Found combined in gypsum, $CaSO_4 + 2H_2O$; in heavy spar, $BaSO_4$; in celestite, $SrSO_4$; in Epsom salts, $MgSO_4 + 7H_2O$; in Glauber salt, $Na_2SO_4 + 10H_2O$, etc.

3. **Formation.**—(*a*) By electrolyzing H_2O, using **Pt** electrodes with pieces of **S** attached (Becquerel, *C. r.*, 1863, **56**, 237). (*b*) By oxidizing **S** or SO_2 in presence of water by **Cl**, **Br**, HNO_3, etc. (*c*) By heating **S** and H_2O to 200°. (*d*) By adding H_2O to SO_3. (*e*) By passing a mixture of SO_2 and **O** over platinum sponge and then adding water.

4. **Preparation.**—Industrially, sulphuric acid is made by utilizing the SO_2 evolved as a by-product in roasting various sulphides—*e. g.*, iron and copper pyrites, blende, etc. (*a*) and (*b*); or by burning sulphur in the air to form the SO_2. The SO_2 is oxidized and converted into sulphuric acid by two distinct processes known as the **contact** and the **chamber** process. In the contact process the SO_2, after careful purification, arsenic especially being removed, is passed together with oxygen through a contact mass

containing finely divided platinum or other catalytic reagent maintained at the proper temperature. The SO_2 unites with the oxygen to form SO_3, which is absorbed in dilute sulphuric acid. This process is especially advantageous for making concentrated or fuming sulphuric acid. In the **chamber** process the SO_2 is passed into a large leaden chamber and brought into contact with HNO_3, steam, and air. The HNO_3 first oxidizes a portion of the SO_2 (*c*); the steam then reacts upon the NO_2, forming HNO_3 and NO (*d*). This NO is at once oxidized again by the air to NO_2, so that *theoretically* no nitric acid is lost, but all is used over again. Practically, traces of it are constantly escaping with the nitrogen introduced as air, so that a fresh supply of nitric acid is needed to make up for this loss. The dilute acid known as chamber acid is concentrated first in lead pans and then in platinum or silica pans. Commercial sulphuric acid known as oil of vitriol has a sp. gr. of 1.83 and contains 93% H_2SO_4; when heated to 338° a 98% acid distills over. The absolute H_2SO_4 cannot be made by evaporation or distillation; it still contains about two per cent of water. It may be made by adding to water, or to the H_2SO_4 containing the two per cent of water, a little more SO_3 or $H_2S_2O_7$ than would be needed to make H_2SO_4; then passing perfectly dry air through it until the excess of SO_3 is removed, leaving absolute H_2SO_4. Fuming pyrosulphuric, or Nordhausen sulphuric acid, $H_2S_2O_7$, is made by solution of sulphuric anhydride in sulphuric acid (*e*); by drying $FeSO_4 + 7H_2O$ until it becomes $FeSO_4 + H_2O$, and then distilling (*f*). Sulphuric anhydride is made by the action of heat on sodium pyrosulphate, $Na_2S_2O_7$ (*g*), prepared by heating $NaHSO_4$ to dull redness; by distilling pyrosulphuric acid, the anhydride is collected in an ice-cooled receiver; by heating H_2SO_4 with P_2O_5 (*h*):

(*a*) $2ZnS + 3O_2 = 2ZnO + 2SO_2$

(*b*) $4FeS_2 + 11O_2 = 2Fe_2O_3 + 8SO_2$

(*c*) $SO_2 + 2HNO_3 = H_2SO_4 + 2NO_2$

(*d*) $3NO_2 + H_2O = 2HNO_3 + NO$

(*e*) $H_2SO_4 + SO_3 = H_2S_2O_7$

(*f*) $4FeSO_4 + H_2O = 2Fe_2O_3 + H_2S_2O_7 + 2SO_2$

(*g*) $Na_2S_2O_7 = Na_2SO_4 + SO_3$

(*h*) $H_2SO_4 + P_2O_5 = 2HPO_3 + SO_3$

Sulphates are made: (*a*) by dissolving the metals in sulphuric acid; (*b*) by dissolving the oxides or hydroxides; (*c*) by displacement. All salts containing volatile acids are displaced by sulphuric acid and a sulphate formed (except the chlorides of mercury). The excess of acid may generally be expelled by evaporation, or the crystals washed with cold water or alcohol. The insoluble sulphates are best made by precipitation.

5. **Solubilities.**—Sulphuric acid is miscible with water in all proportions; the concentrated acid with generation of much heat. Sulphuric acid *transposes the salts of nearly all other acids*, forming sulphates, and either acids (as hydrochloric acid, §269, 4) or the products of their decomposition (as with chloric acid, §273, 6). Chlorides of silver, tin, and antimony are with difficulty transposed by sulphuric acid, and chlorides of mercury not at all. Also, *at temperatures above* about 300° phosphoric and silicic acids (and other acids not volatile at this temperature) transpose sulphates, with vaporization of sulphuric acid.

The sulphates of **Pb**, **Hg′**, **Ba**, **Sr**, and **Ca** are insoluble, those of **Hg′** and **Ca** sparingly soluble. Sulphuric acid and soluble sulphates precipitate solutions of the salts of **Pb**, **Hg′**, **Ba**, **Sr**, and **Ca**; **Hg′** and **Ca** salts incompletely. The metallic sulphates are insoluble in alcohol which precipitates them from their moderately concentrated aqueous solutions. Alcohol added to solutions of the acid sulphates precipitates the normal sulphates, sulphuric acid remaining in solution: $2KHSO_4 = K_2SO_4 + H_2SO_4$. $PbSO_4$ is soluble in a saturated solution of **NaCl** in the cold, depositing after some time crystals of $PbCl_2$, complete transposition being effected. A solution of $PbCl_2$ in **NaCl** is not precipitated on addition of H_2SO_4 (Field, *J. C.*, 1872, **25**, 575).

6. **Reactions.** *A.*—**With metals and their compounds.**—Sulphuric acid, dilute, has no action on **Pb**, **Hg**, **Ag**, **Cu** *, and **Bi**. **Au**, **Pt**, **Ir**, and **Rh** are not attacked by the acid, dilute or concentrated; other metals are attacked by the hot concentrated acid with evolution of SO_2. The following metals: **Sn**, **Th**, **Cd**, **Al**, **Fe**, **Co**, **Ni**, **Mn**, **Zn**, **Mg**, **K**, and **Na** are attacked by the acid of all degrees of concentration; the dilute rapidly and the cold concentrated slowly, with evolution of hydrogen; the hot concentrated with evolution of SO_2. The degree of concentration and the temperature may be regulated so that the two gases may be evolved in almost any desired proportions. A secondary reaction frequently takes place, the metal decomposing the SO_2 forming H_2S or a sulphide; and the H_2S decomposing the SO_2 with separation of sulphur (Ditte, *A. Ch.*, 1890, (6), **19**, 68; Muir and Adie, *J. C.*, 1888, **53**, 47).

Sulphuric acid or soluble sulphates react with soluble **barium** salts to give barium sulphate, white, *insoluble* in hydrochloric or nitric acids. This insolubility is a distinction from all other acids except selenic and fluosilicic. The precipitate formed in the cold is very fine and difficult to separate by filtration; if formed in hot acid solution and then boiled it is retained by a good filter. In dilute solution for complete precipitation the mixture should stand for some time. Solutions of **lead** salts give a

* Andrews, *J. Am. Soc.*, 1896, **18**, 251.

white precipitate of lead sulphate not transposed by acids except H_2S (5), soluble in the fixed alkalies. The presence of alcohol makes the precipitation quantitative (§57, 9). Solution of **calcium** salts not too dilute form a white precipitate of calcium sulphate (§188, 5*c*).

Dilute sulphuric acid does not oxidize any of the lower metallic oxides. Concentrated sulphuric acid is an oxidizing agent. When hot it liberates one atom of oxygen and is reduced to sulphurous acid, which is decomposed with the evolution of sulphur dioxide and water.

The concentrated acid with the aid of heat effects the following changes:

Hg_2O forms mercuric sulphate, and sulphurous anhydride is evolved.

$SnCl_2$ forms, first, sulphurous anhydride, then hydrosulphuric acid, stannic chloride at the same time being produced.

Fe'' is changed to $Fe_2(SO_4)_3$ by hot concentrated sulphuric acid.

Mn''^{+n} forms $MnSO_4$ and O. That is, all compounds of manganese having a degree of oxidation above the dyad are reduced to the dyad with evolution of oxygen.

Potassium permanganate dissolves in *cold concentrated sulphuric acid* with formation of a green solution of a sulphate of the heptad manganese, $(MnO_3)_2SO_4$ (§134, 5*c*).

Similarly the hot concentrated acid also reduces Pb^{IV} to Pb'', Co''' to Co'', Ni''' to Ni'', Fe^{VI} to Fe''', and Cr^{VI} to Cr''', oxygen being liberated (oxidized) and the metal reduced while the bonds of the SO_4 radical are not changed; a sulphate of the metal being produced.

B.—**With non-metals and their compounds.**—When dilute sulphuric acid transposes the salts of other acids, no other change occurs if the acid set free be stable under the conditions of its liberation. In ordinary reactions sulphuric acid never acts as a reducing agent.

1. Many organic acids and other organic compounds are decomposed by the hot concentrated acid, the elements of water being abstracted and carbon set free. Continued heating of the carbon with the hot concentrated acid oxidizes it to CO_2 with liberation of SO_2.

$H_2C_2O_4$ becomes CO_2, CO, and H_2O. The bonds of the H_2SO_4 remain unchanged.

$K_4Fe(CN)_6$ with dilute H_2SO_4 forms **HCN**: $2K_4Fe(CN)_6 + 3H_2SO_4 = 6HCN + K_2FeFe(CN)_6 + 3K_2SO_4$.

Cyanates are decomposed into CO_2 and NH_3: $2KCNO + 2H_2SO_4 + 2H_2O = K_2SO_4 + (NH_4)_2SO_4 + 2CO_2$.

Thiocyanates are also decomposed by concentrated sulphuric acid.

2. **Nitrites** are decomposed with formation of nitric acid and **NO**: $6KNO_2 + 3H_2SO_4 = 3K_2SO_4 + 2HNO_3 + 4NO + 2H_2O$.

3. H_3PO_2 or hypophosphites are oxidized to phosphoric acid with reduction of the sulphuric acid to sulphurous acid and then to sulphur.

4. **Sulphur** is slowly changed by hot concentrated sulphuric acid to sulphurous acid with reduction of the sulphuric acid to the same compound. **Hydrosulphuric acid** with hot concentrated sulphuric acid is oxidized to sulphur with reduction of the sulphuric acid to sulphurous acid. Further oxidation may take place as indicated above.

5. **Chlorates** are transposed and then decomposed when treated with concentrated sulphuric acid: $3KClO_3 + 2H_2SO_4 = 2KHSO_4 + KClO_4 + 2ClO_2 + H_2O$.

6. **HBr** forms **Br** and SO_2. No action except in concentrated solution.

7. **HI** forms **I** and SO_2.

7. **Ignition.**—All sulphates fused with a fixed alkali carbonate are transposed to carbonates (oxide or metal if the carbonate is decomposed by the heat used, §228, 7) with formation of a fixed alkali sulphate (method of analysis of insoluble sulphates). If the sulphate, or any other compound containing sulphur, is fused in the presence of carbon, as fusion with a fixed alkali carbonate on a piece of charcoal, the resulting mass contains an alkali sulphide, which, when moistened, blackens metallic silver.

The sulphates of **Cu**, **Sb**, **Fe**, **Hg**, **Ni** and **Sn** are completely decomposed at a red heat: $2FeSO_4 = Fe_2O_3 + SO_3 + SO_2$; $2CuSO_4 = 2CuO + 2SO_2 + O_2$. A white heat decomposes the sulphates of **Al**, **Cd**, **Ag**, **Pb**, **Mn** and **Zn**. An ordinary white heat has no action on the sulphates of the alkalis and alkaline earths; but at the most intense heat procurable the sulphates of **Ba**, **Ca** and **Sr** are changed to oxides; and at the same temperature K_2SO_4 and Na_2SO_4 are completely volatilized, preceded by partial decomposition.

Lead sulphate heated in a current of hydrogen is reduced according to the following equation: $2PbSO_4 + 6H_2 = Pb + PbS + SO_2 + 6H_2O$. After a distinct interval the remainder of the sulphur is removed as H_2S: $PbS + H_2 = Pb + H_2S$ (Rodwell, *J. C.*, 1863, **16**, 42). Potassium sulphate heated in a current of hydrogen is reduced to potassium acid-sulphide: $K_2SO_4 + 4H_2 = KOH + KHS + 3H_2O$ (Berthelot, *A. Ch.*, 1890, (6), **21**, 400). Potassium acid-sulphate, $KHSO_4$, heated to 200° evolves H_2SO_4. The sodium acid-sulphate decomposes more readily.

8. **Detection.**—Free sulphuric acid or the soluble sulphates are detected by precipitation in hot hydrochloric acid solution with barium chloride, forming the white, granular, insoluble barium sulphate.

The sulphates insoluble in water are decomposed for analysis—(1st) by long boiling with solution of **alkali carbonate**; and more readily (2d) by fusion with an alkali carbonate. In both cases there are produced—alkali *sulphates* soluble in water, and *carbonates* soluble by hydrochloric or nitric acid, *after* removing the sulphate (*a*). If the fusion be done on charcoal, more or less deoxidation will occur, reducing a part or the whole of the

sulphate to sulphide (7), and the carbonate to metal (as with lead, §57, 7), or leaving the metal as a carbonate or oxide (7, §§222 and 228).

a. $BaSO_4 + Na_2CO_3 = Na_2SO_4$ (soluble in water) + $BaCO_3$ (soluble in acid).

A mixture of H_2SO_4 and a sulphate may be separated by strong alcohol, which precipitates the latter. A test for free *sulphuric acid, in distinction from sulphates*, may be made by the use of **cane sugar**, as follows: A little of the liquid to be tested is concentrated on the water-bath; then from two to four drops of it are taken on a piece of porcelain, with a small fragment of white sugar, and evaporated to dryness by the water-bath. A greenish-*black* residue indicates sulphuric acid. (With the same treatment, hydrochloric acid gives a brownish-black, and nitric acid a yellow-brown residue.) A strip of white glazed paper, wet with the liquid tested, by immersing it several times at short intervals, then dried in the oven at 100°, will be colored black, brown or reddish, if the liquid contains as much as 0.2 per cent of sulphuric acid.

9. **Estimation.**—(*a*) By precipitation as barium sulphate and weighing as such. The solution should be hot and acidified with hydrochloric acid, and the mixture should be boiled a few minutes after the addition of the barium chloride. (*b*) By precipitation as barium sulphate with an excess of an hydrochloric acid solution of barium chromate (three per cent hydrochloric acid). Add NH_4OH, fill to a definite volume, and filter through a dry filter-paper. Transfer an aliquot portion to an azotometer with H_2O_2, and after acidifying, determine the oxygen evolved (Baumann, *Z. angew.*, 1891, 140) (§244, 64, *12*). (*c*) When present in small amounts in drinking water by a photometric method (Hinds, *C. N.*, 1896, **73**, 285 and 299).

§267. Persulphuric acid. $HSO_4 = 97.068$.

1. **The anhydride.**—The anhydride, S_2O_7, was discovered by Berthelot (*C. r.*, 1878, **86**, 20 and 71). It is obtained by the action of the silent electric discharge upon a mixture of equal volumes of dry SO_2 and O. At 0°, it consists of flexible cyrstalline needles, remaining stable for several days. When heated it decomposes into SO_3 and O. With SO_2 it combines to form SO_3: $S_2O_7 + SO_2 = 3SO_3$. Although in its reactions it acts as a strong oxidizing agent, it is weaker than chlorine or ozone; oxalic acid and chromium salts are not oxidized (Traube, *B.*, 1889, **22**, 1518, 1528; 1892, **25**, 95).

2. **The Acid.**—The acid was first prepared by Marshall, who electrolyzed cold fairly dilute sulphuric acid (*J. C.*, **59**, 771). Hydrogen is liberated at the cathode while the HSO_4 anions discharged at the anode unite to form persulphuric acid, the following reaction taking place.

$$2H_2SO_4 = H_2 + H_2S_2O_8.$$

The acid may also be formed by the action of H_2O_2 on concentrated H_2SO_4. Water solutions of the acid decompose very rapidly. Solutions of the acid, in concentrated sulphuric acid, are more stable.

3. **Salts.**—The potassium salt, $K_2S_2O_8$, is prepared by the electrolysis of a saturated solution of $KHSO_4$ with a current of 3 to 3.5 amperes. It is a white crystalline powder, which may be recrystallized from hot water with almost no decomposition. Continued heating of the solution effects decomposition. One hundred parts of water dissolve 0.564 part of the salt at 0° and 4.08 parts at 40°.

The ammonium salt is prepared by the electrolysis of a saturated solution of ammonium sulphate. One hundred parts of water dissolve 58.2 parts of the salt at 0°. It can be recrystallized from water if the solution not heated above 60°. It forms monoclinic crystals. The dry salt is stable at 100°. It is used in the cyanide process for the recovery of gold (Elbs, *Z. angew.*, 1897, 195). The potassium is the least soluble of the persulphate salts. A solution of K_2CO_3 gives an abundant crystalline precipitate of $K_2S_2O_8$ from a solution of the ammonium salts. The barium salt, $BaS_2O_8.4H_2O$, is fairly soluble and may be prepared by rubbing the ammonium salt with barium hydroxide.

3. **Reactions.**—All persulphates when dissolved in water are decomposed slowly in the cold and more rapidly on heating, oxygen, free sulphuric acid and a sulphate being formed.

$$2K_2S_2O_8 + 2H_2O = 2K_2SO_4 + 2H_2SO_4 + O_2 .$$

A large proportion of the oxygen escapes as ozone, which may be identified by its odor and action on starch iodide paper. Ammonium persulphate in water solution decomposes slowly at the ordinary temperature without the evolution of oxygen.

$$8(NH_4)_2S_2O_8 + 6H_2O = 14NH_4HSO_4 + 2H_2SO_4 + 2HNO_3 .$$

Persulphates act as strong oxidizing agents. Salts of Ag', Mn'', Co'', Ni'' and Pb'' ore oxidized in the presence of alkalies to the peroxides of these metals.

If ammonia and a little silver nitrate are added to a strong solution of ammonium persulphate, nitrogen is rapidly evolved and the solution becomes heated to boiling. The silver peroxide first formed oxidizes the ammonia with liberation of nitrogen. (*Z. Phys. Ch.*, **37**, 255, 1901.)

Fe'' and Ce''' are oxidized to Fe''' and Ce'''' salts. **KI** is rapidly oxidized; $K_4Fe(CN)_6$ becomes $K_3Fe(CN)_6$; Alcohol is slowly oxidized to aldehyde, rapidly on warming; organic dyes are slowly bleached.

4. **Caro's Acid.**—By adding a solid persulphate to concentrated sulphuric acid at 0°, a solution is obtained possessing strong oxidizing properties. It may also be obtained by adding 30 per cent hydrogen peroxide (perhydrate) to concentrated sulphuric acid:

$$H_2SO_4 + H_2O_2 = H_2O + H_2SO_5 .$$

The acid H_2SO_5 is known as monopersulphuric acid [*Z. angew.*, **1898**, 845; *Ber.*, **34**, 853 (1901); **41**, 1839 (1909)].

5. **Detection.**—Persulphates are tested for by their oxidizing properties and formation of the peroxides of some metals. They are distinguished from hydrogen peroxide by the fact that persulphates do not decolorize potassium permanganates and do not produce a yellow color with titanium sulphate.

§268. Chlorine. $Cl = 35.46$. Valence one, three, four, five, and seven.

1. **Properties.**—*Molecular weight*, 70.92. *Vapor density*, 35.8. The molecule contains two atoms, Cl_2. Under ordinary air pressure it liquefies at −33.6° and solidifies at —102° (Olszewski, *M.*, 1884, **5**, 127). Under pressure of six atmospheres it liquefies at 0°. It is a greenish-yellow, suffocating gas, not combustible in oxygen, burns in hydrogen (in sunlight combines explosively), forming **HCl**. On cooling an aqueous solution of the gas to 0°, crystals of $Cl_2.10H_2O$ separate out (Faraday, *Quart. Jour. of Sci.*, 1823, **15**, 71). Chlorine when passed into a solution of **KOH** produces, if cold, **KCl** and **KClO**, if hot, **KCl** and $KClO_3$: $2KOH + Cl_2 = KCl + KClO + H_2O$; $6KOH + 3Cl_2 = 5KCl + KClO_3 + 3H_2O$. Passed into an excess of NH_4OH, NH_4Cl and **N** are formed: $8NH_4OH + 3Cl_2 = 6NH_4Cl + N_2 + 8H_2O$; if chlorine be in excess chloride of nitrogen is formed: $NH_4OH + 3Cl_2 = NCl_3 + 3HCl + H_2O$. The NCl_3 is one of the most dangerous explosives known; hence chlorine should never be passed into NH_4OH or into a solution of ammonium salts without extreme caution. Chlorine bleaches litmus, indigo and most other organic coloring matter.

The three elements, chlorine, bromine and iodine, resemble each other in almost all their properties, reactions and combinations, differing (as do their atomic weights, 35.45, 79.95, 126.85) with a regular progressive variation; so that their compounds present themselves to us as members of progressive series. In several particulars fluorine (atomic weight, 19.05) corresponds to the first member of this series (§13).

Two oxides of chlorine have been isolated: Cl_2O, hypochlorous anhydride (§270), and ClO_2, chlorine dioxide. The latter is made by the addition of H_2SO_4 to $KClO_3$ at 0°. It is a yellowish-green gas, condensing at 0° to a red-brown liquid. At —59° it becomes a crystalline solid, resembling $K_2Cr_2O_7$. It may be preserved in the dark, but becomes explosive in the sunlight.

The most important acids containing chlorine are discussed under the sections following. They are:

Hydrochloric acid, HCl.

Hypochlorous acid, $HClO$.

Chlorous acid, $HClO_2$.

Chloric acid, $HClO_3$.

Perchloric acid, $HClO_4$.

2. **Occurrence.**—It does not occur free in nature, but its salts are numerous, the most abundant being $NaCl$.

3. **Formation.**—(*a*) By the action of HCl upon higher oxides as indicated in §269, 6*A*. The usual class-room or laboratory method is illustrated by the following equations:

$$MnO_2 + 4HCl = MnCl_2 + Cl_2 + 2H_2O$$

$$MnO_2 + 2NaCl + 3H_2SO_4 = MnSO_4 + 2NaHSO_4 + Cl_2 + 2H_2O$$

(*b*) By fusing together NH_4NO_3 and NH_4Cl : $4NH_4NO_3 + 2NH_4Cl = 5N_2 + Cl_2 + 12H_2O$. (*c*) By ignition of dry $MgCl_2$ in the air: $2MgCl_2 + O_2 = 2MgO + 2Cl_2$ (Dewar, *J. Soc. Ind.*, 1887, **6**, 775). (*d*) Some chlorides are dissociated by heat alone: $2AuCl_3 = 2Au + 3Cl_2$.

4. **Preparation.**—(*a*) *Weldon's process*: MnO_2 is treated with HCl, and the $MnCl_2$ formed is precipitated as $Mn(OH)_2$ by adding $Ca(OH)_2$. The $Mn(OH)_2$ is warmed by steam, and air is blown into it, oxidizing it again to MnO_2, and by repeating this process the same manganese is used over again. See Lunge and Prett (*Z. angew.*, 1893, 99) for modification of this method, using HNO_3. (*b*) *Deacon's process*: HCl, mixed with air, is passed over fire-bricks moistened with $CuCl_2$ and heated to about 440°. The heat first changes the $CuCl_2$ to $CuCl$, evolving chlorine; then the oxygen of the air, aided by the HCl, oxidizes the $CuCl$ to $CuCl_2$. It is not certain that the explanation is correct. It is only known that the hydrochloric acid which is passed into the apparatus comes out as free chlorine, and that the copper chloride (small in amount) does not need renewing. (*c*) *Electrolytic process:* Chlorine is very largely produced as a by-product in the manufacture of caustic soda by the electrolysis of common salt. A number of processes have been developed in some of which the fused salt is electrolyzed while in others the electric current is passed through strong brine.

5. **Solubilities.**—The maximum solubility of chlorine in water is at 10°. At 0° one volume of water dissolves 1.5 volumes of chlorine; at 10° three volumes; at 30° 1.8 volumes (Riegel and Walz, *J.*, 1846, 72). Boiling completely removes the chlorine from water. The chlorine acts upon the water to a small extent, forming hydrochloric and hypochlorous acid:

$$Cl_2 + H_2O \leftrightarrows \overset{+}{H}\,\overset{-}{Cl} + \overset{+}{H}\,\overset{-}{ClO}$$

The reaction is reversible, but if an alkali is present the hydrogen ions are removed and all of the chlorine reacts with the water:

$$Cl_2 + H_2O + 2\overset{-}{O}H = \overset{-}{Cl} + \overset{-}{Cl}O + 2H_2O$$

Only chlorides and hypochlorites remain in solution. On acidifying the solution the chlorine is again liberated.

6. **Reactions.** *A.*—**With metals and their compounds.**—Chlorine is one of the most powerful oxidizing agents known, becoming always a chloride or hydrochloric acid. All metals are attacked by moist chlorine, forming chlorides, many of them combining with vivid incandescence. With perfectly dry chlorine many of the metals are not at all attacked. **Sn**, **Sb**, and **As** are rapidly attacked, forming liquid chlorides (Cowper, *J. C.*, 1883, **43**, 153; Veley, *J. C.*, 1894, **65**, 1). In the presence of acids the oxidation of the metal takes place to the same degree as when that metallic compound is acted upon by **HCl** (§**269**, 6*A*); a chloride is formed having the same metallic valence that would have resulted from treating the oxide or hydroxide with hydrochloric acid, *e. g.*, adding **HCl** to Co_2O_3 makes $CoCl_2$ not $CoCl_3$, hence adding chlorine to metallic cobalt makes $CoCl_2$ and not $CoCl_3$. In alkaline mixture usually the highest degree of oxidation possible is attained, as indicated by the following:

1. **Pb**″ becomes PbO_2 and a chloride in alkaline mixture. With $PbCl_2$, it is claimed that the unstable $PbCl_4$ is formed (Sobrero and Selmi, *A. Ch.*, 1850, (3), **29**, 162; Ditte, *A. Ch.*, 1881, (5), **22**, 566).

2. **Hg**′ becomes **Hg**″ in acid and in alkaline mixture; also **HCl** or a chloride.

3. **As**‴ becomes As^V in acid and in alkaline mixture. Some water must be present or the reverse action takes place, forming $AsCl_3$ (§**269**, 6*A*2).

4. **Sb**‴ becomes Sb^V and a chloride with acids and alkalis.

5. **Sn**″ becomes Sn^{IV} and a chloride with acids and alkalis.

6. Mo^{VI-n} becomes Mo^{VI} and a chloride with acids and alkalis.

7. **Bi**‴ becomes Bi^V and a chloride with alkalis only.

8. **Cu**′ becomes **Cu**″ and a chloride with alkalis and with acids.

9. **Cr**‴ becomes Cr^{VI} and a chloride in alkaline mixture only.

10. **Fe**″ becomes **Fe**‴ and a chloride with acids and alkalis, but with alkalis it is also further oxidized to a ferrate.

11. **Co**″ becomes $Co(OH)_3$ and a chloride with alkalis only.

12. **Ni**″ becomes $Ni(OH)_3$ and a chloride with alkalis only.

13. **Mn**″ becomes MnO_2 and a chloride with alkalis only. See Ditte, *l. c.*, for formation of $MnCl_4$.

B.—**With non-metals and their compounds.**

1. $H_2C_2O_4$ in acid mixture: $H_2C_2O_4 + Cl_2 = 2CO_2 + 2HCl$, the $H_2C_2O_4$ must be in excess and hot (Guyard, *Bl.*, 1879, (2), **31**, 299); in alkaline mixture: $K_2C_2O_4 + 4KOH + Cl_2 = 2K_2CO_3 + 2KCl + 2H_2O$.

HCN becomes **CNCl** and **HCl** (Bischoff, *B.*, 1872, **5**, 80).

HCNS forms NH_3, H_2SO_4, CO_2, and other variable products, and **HCl** (Liebig, *A.*, 1844, **50**, 337).

$H_4Fe(CN)_6$ becomes $H_3Fe(CN)_6$ and **HCl**; an excess of **Cl** finally decomposes the $H_3Fe(CN)_6$.

2. Chlorine does not appear to have any oxidizing action upon the oxides or acids of **nitrogen.**

3. **Phosphorus** and all lower oxidized forms become H_3PO_4 with formation of **HCl**.

4. **Sulphur** and all its lower oxidized forms are oxidized to H_2SO_4 with formation of **HCl**. In an alkaline solution a sulphate and a chloride are formed. With H_2S, **S** is first deposited, which an excess of **Cl** oxidizes to H_2SO_4. A sulphide in an alkaline mixture is at once oxidized to a sulphate without apparent intermediate liberation of sulphur.

5. In alkaline mixture chlorine oxidizes **chlorites**, and **hypochlorites** to chlorates with formation of a chloride: $KClO_2 + 2KOH + Cl_2 = KClO_3 + 2KCl + H_2O$. With **NaOH** a hypochlorite is formed if cold, if hot a chlorate:

$$2NaOH + Cl_2 = NaClO + NaCl + H_2O$$
$$6NaOH + 3Cl_2 = NaClO_3 + 5NaCl + 3H_2O$$

6. Chlorine does not oxidize **bromine** in acid mixture, in alkaline mixture a bromate and a chloride are formed. **HBr** in acid solution becomes *free bromine,* in alkaline mixture a *bromate*; hydrochloric acid or a chloride being formed.

7. **Iodine** is oxidized to HIO_3 in acid mixture, forming **HCl**: in an alkaline mixture a *periodate* and a chloride are formed. From **hydriodic acid** or **iodides,** iodine is first liberated, followed by further oxidation as indicated above: $2HI + Cl_2 = 2HCl + I_2$: $I_2 + 5Cl_2 + 6H_2O = 2HIO_3 + 10HCl$; $KI + 8KOH + 4Cl_2 = KIO_4 + 8KCl + 4H_2O$.

By comparing the oxidizing action of **Cl** with that of **Br** and **I**, the following facts will be observed, and should be carefully considered. The elements chlorine, bromine, and iodine have an oxidizing power in reverse order of their atomic weights, chlorine being the strongest. That is, if all three have the same oxidizing effect, the chlorine acts with the greatest rapidity; and in some cases, as with cuprous salts, the chlorine oxidizes while the iodine does not. Their hydracids are reducing agents graded in the reverse order. If any increase of bonds takes place in presence of an acid, by chlorine, bromine or iodine, the same increase always occurs in presence of a fixed alkali. But the oxidation frequently goes further in presence of a fixed alkali. Thus, with chlorine and potassium hydroxide we form PbO_2, $Ni(OH)_3$, Bi_2O_5, $Co(OH)_3$, K_2FeO_4, and MnO_2, which cannot be formed in presence of an acid.

It is very important to remember that *those oxides which are formed by chlorine, in presence of a fixed alkali, but not in presence of an acid, are the only ones which can be reduced by hydrochloric acid. And further, that this reduction proceeds not always to the original form, never proceeding beyond that number of bonds capable of being formed in presence of an acid.* Thus,

any lead salt, with potassium hydroxide and chlorine, forms PbO_2, and this treated with hydrochloric acid again forms the lead salt, $PbCl_2$. And ferrous chloride with potassium hydroxide and chlorine forms K_2FeO_4, in which iron is a true hexad, and K_2FeO_4 with hydrochloric acid forms, not the ferrous chloride with which we began, but ferric chloride, for it could only be oxidized to that point in presence of an acid.

The above is true for bromine and iodine, as well as for chlorine.

7. **Ignition.**—See 1.

8. **Detection.**—Free chlorine is recognized by its odor, by its liberation of iodine from potassium iodide, by its bleaching action upon litmus, indigo, etc., and by its action as a powerful oxidizing agent (see above).

Chlorine acts on metallic mercury in the cold, producing the insoluble mercurous chloride:

$$2Hg + Cl_2 = 2HgCl.$$

As hydrochloric acid does not act upon metallic mercury it may be separated from chlorine by this reaction, the mixture being shaken with mercury until the chlorine is removed. Silver nitrate precipitates one-sixth of the chlorine as chloride:

$$3Cl_2 + 6AgNO_3 + 3H_2O = 5AgCl + AgClO_3 + 6HNO_3.$$

9. **Estimation.**—(*a*) It is added to a solution of potassium iodide and the liberated iodine determined by standard sodium thiosulphate. (*b*) It is converted into a chloride by reducing agents, and estimated by the usual methods (**§269,** 8).

§269. Hydrochloric Acid. $HCl = 36.468$.

$H'Cl^{-\prime}$, H—Cl.

1. **Properties.**—*Vapor density,* 18.22. At ordinary pressure it liquefies at −82.9° and solidifies at −112.5° (Weber, *Z. Anorg.*, **74,** 297; 1912). At 10° under pressure of 40 atmospheres it condenses to a colorless liquid (Faraday, *Tr.*, 1845, 155). *Critical temperature,* 52.3°; *critical pressure,* 86 atmospheres (Dewar, *C. N.*, 1885, **51,** 27). Dissociated into **H** and **Cl** at about 1500°, but combines again upon cooling (Deville, *C. r.*, 1865, **60,** 317). It is a colorless gas, having an acrid, irritating odor. Readily absorbed by water. The chemically pure concentrated acid has usually a specific gravity of 1.20, and contains 39.11 per cent **HCl** (Lunge and Marchlewski, *Z. angew.*, 1891, **4,** 133). The U. S. P. acid has a *specific gravity* of 1.163 at 15° and contains 31.9 per cent **HCl**. A concentrated solution of **HCl** gives off gaseous **HCl** faster than H_2O; a dilute solution gives off H_2O faster than **HCl**, as a final result in both cases an acid *sp. gr.* 1.1 distils unchanged at 110° and contains 20.18 per cent **HCl** (Bineau, *A. Ch.*, 1843, (3), **7,** 257).

2. **Occurrence.**—Found native only in the vicinity of volcanoes. Found as a chloride in many minerals, sodium chloride being the most abundant.

3. **Formation.**—(*a*) All chlorides except those of mercury are transposed by H_2SO_4; silver chloride must be heated nearly to the boiling point of the H_2SO_4 before the action begins. Lead, antimony and tin chlorides are slowly transposed.

(*b*) By the action of sunlight on a mixture of **H** and **Cl**, or by heating the mixture to 150°. (*c*) Platinum black, palladium, charcoal, and some other substances which rapidly absorb gases will cause the union of the hydrogen and the chlorine. (*d*) When hydrogen is passed over the heated chlorides of the most of the metals of the first four groups, the metals are set free and hydrochloric acid is formed. (*e*) Slowly formed by the action of chlorine upon water in the sunlight; rapidly by its action upon reducing acids such as $H_2C_2O_4$, HH_2PO_2, H_2S, H_2SO_3, etc.: $HH_2PO_2 + 2Cl_2 + 2H_2O = H_3PO_4 + 4HCl$.

Chlorides may be made: (*a*) By direct union of the elements, mostly without heat. Whether an *ous* or *ic* salt is formed depends upon the amount of chlorine used. (*b*) By the action of hydrochloric acid upon the corresponding oxides, hydroxides, carbonates, or sulphites. The solutions formed may be evaporated to expel excess of acid. If the chlorides thus formed contain water of crystallization it cannot be removed by heat alone, for part of the acid is by this means driven off, and a basic salt remains. If the anhydrous chloride is desired, it may always be made by (*a*), and when thus formed may be sublimed without decomposition. (*c*) Chlorides of the first group are best made by precipitation. (*d*) Metals soluble in hydrochloric acid evolve hydrogen and form chlorides. In these cases *ous*, and not *ic*, salts are formed. (*e*) Many chlorides may be formed by bringing $HgCl_2$ in contact with the hot metal.

4. **Preparation.**—For commercial purposes, made by treating **NaCl** with H_2SO_4 and distilling.

5. **Solubilities.**—Hydrochloric acid (gas) is very soluble in water as stated in (1); forming in its solutions of various strengths the hydrochloric acid of commerce. Its combinations with metals, forming chlorides, are for the most part soluble in water. **AgCl** and **HgCl** are insoluble in water. $PbCl_2$ is only slightly soluble in cold water (§57, 5*c*). **These three chlorides** constitute the **first** or **silver group** of **metals**, and are precipitated from their solutions by **hydrochloric acid** or **soluble chlorides** (§61). The following chlorides not commonly met with are insoluble: cuprous chloride **CuCl**, aurous chloride **AuCl**, thallous chloride **TlCl** and platinous chloride, $PtCl_2$. The following oxychlorides are insoluble: **BiOCl**, **SbOCl** and Hg_2Cl_2O. Solutions of lead salts are not precipitated by mercuric chloride; green chromic chloride is incompletely precipitated and a sulphuric acid solution of molybdenum oxychloride not at all by silver nitrate. The chlorides of **Sb'''**, **Sn''**, and **Bi** require the presence of some free acid to keep them in solution. $AsCl_3$, PCl_3, $SbCl_5$ and $SnCl_4$ are liquids at ordinary temperature. The first two are decomposed by water liberating **HCl**: $AsCl_3 + 3H_2O = H_3AsO_3 + 3HCl$. A saturated solution of bismuth nitrate is precipitated by **HCl** as the oxychloride (§76, 6*f*) which is readily soluble in excess of **HCl**. Hydrochloric acid increases the solubility of the chlorides of **Pb**, **Hg**, **Ag**, **Sb**, **Au**, **Pt**, **Bi** and **Cu'**; it decreases the solubility of **Cd**, **Cu''**, **Co**, **Ni**, **Mn**, **Th**, **Ba**, **Sr**,

Ca, **Mg**, **Au**, **K** and NH_4. Chlorides of **Th**, **Ba**, **Na**, **K** and NH_4 are nearly insoluble in strong **HCl** (Ditte, *C. r.*, 1881, **92**, 242; *A. Ch.*, 1881, (5), **22**, 551; Berthelot, *A. Ch.*, 1881, (5), **23**, 86). Chlorides of **Li**, **Ca** and **Sr** are soluble in absolute alcohol or amyl alcohol.

Silver chloride is readily soluble in ammonium hydroxide (separation from lead and mercurous chlorides) (§**59**, 6*a*); lead chloride is soluble in fixed alkali hydroxides (§**57**, 6*a*).

HCl dissolves or transposes all insoluble oxalates, carbonates, hypophosphites, phosphates, and sulphites. Sulphides of **Fe**″, **Mn**, and **Zn** are dissolved readily; those of **Pb**, **Ag**, **Sb**, **Sn**, **Bi**, **Cu**, **Cd**, **Co**, and **Ni** if the acid be concentrated; As_2S_3 and As_2S_5 are insoluble in the cold concentrated acid, very slowly soluble in the hot concentrated acid; **HgS**, red, is insoluble; black, very slowly soluble in the hot concentrated acid. $HgSO_4$ is only partially transposed by **HCl** (§**58**, 6*f*), $BaSO_4$ not at all. The insoluble sulphates of **Pb**, **Hg**′, **Sr**, and **Ca** are slowly but completely dissolved by the hot concentrated acid. Many of the metallic chlorides are soluble in alcohol, a few are soluble in ether.

6. **Reactions.**—*A.*—**With metals and their compounds.**—Hydrochloric acid acts upon the following metals, forming chlorides with evolution of hydrogen: **Pb** (slowly but completely), **Sn**, **Cu** (very slowly), **Cd**, **Fe**, **Cr**, **Al**, **Co**, **Ni**, **Mn**, **Zn**, and the metals of the fifth and sixth groups: **Ag**, **Hg**, **As**, **Sb**, **Au**, **Pt**, and **Bi** are insoluble in **HCl** (Ditte and Metzner, *A. Ch.*, 1893, (6), **29**, 389).

The following metallic oxides and hydroxides are acted upon by hydrochloric acid, forming chlorides of the metal without reduction, water being the only by-product: **Pb**″, **Ag**, **Hg**, **As**‴ (only with very concentrated acid), **Sb**, **Sn**, **Au**‴, **Pt**, Mo^{VI}, **Bi**‴, **Cu**, **Cd**, **Fe**, **Al**, **Cr**‴, **Co**″, **Ni**″, **Mn**″, **Zn**, **Ba**, **Sr**, **Ca**, **Mg**, **K**, and **Na**. The ignited oxides unite with **HCl** more slowly than when freshly precipitated or when dried at 100°. Ignited Cr_2O_3 is insoluble in **HCl**: other ignited oxides, as Fe_2O_3, Al_2O_3, etc., require very long continued boiling with the **HCl** to effect solution.

The following metallic compounds are attacked by hydrochloric acid with reduction of the metal and evolution of chlorine:

1. $Pb^{''+n}$ becomes $PbCl_2$; no action with a chloride in presence of a three per cent solution of acetic acid, while bromine is completely set free from a bromide by PbO_2 in presence of three per cent of acetic acid (detection of a chloride in presence of a bromide) (Vortmann, *M.*, 1882, **3**, 510; *B.*, 1887, **15**, 1106).

2. As^{V} becomes $AsCl_3$. (The presence of very concentrated **HCl** is required; Fresenius, *Z.*, 1862, **1**, 448; Smith, *J. Am. Soc.*, 1895, **17**, 682 and 735.)

3. Bi^{V} becomes $BiCl_3$.

4. Cr^{VI} becomes $CrCl_3$. With $K_2Cr_2O_7$, bromine is completely liberated from a bromide in presence of 4 cc. of H_2SO_4 to 100 cc. of water. The chlorine of a chloride is not liberated, and the bromine may be removed by boiling. Test the solution for a chloride (Dechan, *J. C.*, 1886, **49**, 682). Dry HCl does not reduce Cr^{VI} but combines with it to form the volatile CrO_2Cl_2, chlorochromic anhydride (method of detecting a chloride in the presence of a bromide).

5. With the exception of ferrates the salts of iron are not reduced by hydrochloric acid.

6. $Co^{''+n}$ becomes $CoCl_2$.

7. $Ni^{''+n}$ becomes $NiCl_2$.

8. $Mn^{''+n}$ becomes $MnCl_2$. MnO_2 with small amounts of dilute H_2SO_4 (1-10) may be used to detect a chloride in presence of an iodide or bromide. Boiling the mixture removes the iodine first, then the bromine; while the chlorine is not set free until considerable H_2SO_4 has been added (Jones, *C. N.*, 1883, **48**, 296). A mixture of $KHSO_4$ and $KMnO_4$ completely liberates the bromine from a bromide in the cold. A chloride remains undecomposed until warmed. Aspirate off the bromine, warm and collect the chlorine (Berglund, *Z.*, 1885, **24**, 184).

B.—**With non-metals and their compounds.**

1. No reducing action with $H_2C_2O_4$, H_2CO_3, HCN, HCNS, $H_4Fe(CN)_6$, and $H_3Fe(CN)_6$.

2. HNO_2 forms chiefly NO and Cl. HNO_3 forms NO_2Cl and Cl, or NOCl and Cl, or merely NO_2 and Cl. In case excess of HCl is used the reaction is: $2HNO_3 + 6HCl = 2NO + 3Cl_2 + 4H_2O$ (Koninck and Nihoul, *Z. anorg.*, 1890, 477). Dry HCl gas, passed into a cold mixture of concentrated H_2SO_4 and HNO_3, reacts according to the following equations: $2HCl + 2HNO_3 = 2H_2O + 2NO_2 + Cl_2$ (Lunge, *Z. angew.*, 1895, 4, 8, and 11).

3. No reducing action with H_2S, H_2SO_3, or H_2SO_4. With thiosulphates the unstable $H_2S_2O_3$ is liberated which decomposes as follows: $2Na_2S_2O_3 + 4HCl = 4NaCl + S_2 + 2SO_2 + 2H_2O$. Sulphates of Ag and Hg′ are completely transposed by HCl, those of Ba, Sr, and Ca not at all, all others partially (Prescott, *C. N.*, 1877, **36**, 179).

4. With an excess of HCl, hypophosphites, phosphites, and phosphates are dissolved or transposed without reduction.

5. Hypochlorous acid forms chlorine and water: $HClO + HCl = H_2O + Cl_2$. Chloric acid forms ClO_2, Cl_2O, and Cl in varying proportions, but with HCl in excess the following reaction takes place: $KClO_3 + 6HCl = KCl + 3Cl_2 + 3H_2O$ (Koninck and Nihoul, *Z. anorg.*, 1890, 481).

6. $KBrO_3$ is decomposed by boiling with **HCl**, the bromine being set free: $2KBrO_3 + 12HCl = 2KCl + Br_2 + 5Cl_2 + 6H_2O$ (Kaemmerer, *J. pr.*, 1862, **85**, 452).

7. With HIO_3, ICl_3 and **Cl** are formed, no action in dilute solutions: $HIO_3 + 5HCl = ICl_3 + Cl_2 + 3H_2O$ (Ditte, *A.*, 1870, **156**, 336). According to Bugarsky (*Z. anorg.*, 1895, **10**, 387) KHI_2O_6 with dilute H_2SO_4 does not liberate chlorine from a chloride even on boiling (separation from a bromide).

7. **Ignition.**—The chlorides of metals are, generally, more volatile than the other compounds of the same metals: example, ferric chloride.

Insoluble chlorides are readily transposed by fusion with sodium carbonate: $PbCl_2 + Na_2CO_3 = PbO + 2NaCl + CO_2$. If the carbonate be mixed with charcoal, or if the fusion is done on a piece of charcoal, the metal is also reduced: $2PbCl_2 + 2Na_2CO_3 + C = 2Pb + 4NaCl + 3CO_2$.

Heated in a bead of microcosmic salt, previously saturated with copper oxide in the inner blow-pipe flame, chlorides impart a *blue color* to the outer flame, due to copper chloride.

Dry sodium sulphate at 150° is transposed by dry **HCl** (Colson, *C. r.*, 1897, **124**, 81). Gaseous **HCl** transposes potassium and sodium sulphates completely at a dull-red heat. With the sulphates of the alkaline earths the transposition is nearly complete (Hensgen, *B.*, 1876, **9**, 1671). The silver halides heated with bismuth sulphide on charcoal before the blow-pipe give distinguishing colored incrustations: **AgI**, bright red; **AgBr**, deep yellow; **AgCl**, white (Goldschmidt, *C. C.*, 1876, 297).

8. **Detection.**—(*a*) In its soluble compounds, when not in mixtures with bromides and iodides, hydrochloric acid is readily detected by precipitation with solution of silver nitrate, as a white curdy precipitate, opalescence if only a trace be present, turning gray on exposure to the light.

The properties of the precipitate of *silver chloride* are given in §**59**, 5*c* and 6*f*. It is of analytical interest in that it is freely soluble in **ammonium hydroxide** (considerably more freely than the bromide, and far more freely than the iodide of silver); soluble in hot, concentrated solution of **ammonium carbonate** (which dissolves traces of bromide, and no iodide of silver); insoluble in nitric acid, temporarily soluble in strong hydrochloric acid, precipitating again on dilution. It should be observed, that it is appreciably soluble in solutions of chlorides.

(*b*) A test for *traces of free hydrochloric acid*, in distinction from metallic chlorides, is made by heating the solution with MnO_2, without adding an acid, and distilling into a solution of potassium iodide and starch. Larger proportions of **HCl** are more frequently separated by distilling it intact.

(*c*) Gaseous hydrochloric acid (formed by adding sulphuric acid to dry chlorides, 3*a*) is readily detected by the white fumes formed when brought in contact with ammonia vapor. Also by bringing a stirring rod moistened with silver nitrate in contact with the hydrochloric acid gas. Con-

firm by proving the solubility of the white precipitate in ammonium hydroxide.

(*d*) The reaction with *chromic anhydride* is in use as a test for hydrochloric acid, more especially in presence of bromides:

(*a*) $2HCl + CrO_3 = CrO_2Cl_2$ (chlorochromic anhydride) $+ H_2O$

(*b*) $4NaCl + K_2Cr_2O_7 + 3H_2SO_4 = 2CrO_2Cl_2 + 2Na_2SO_4 + K_2SO_4 + 3H_2O$

To obtain a rapid production of the gas, so that it may be recognized by its color, the operation may be made as follows: Boil a mixture of solid **potassium dichromate** and **sulphuric acid**, in an evaporating-dish until bright red, and then add the substance * to be tested, in powder — obtained, if necessary, by evaporation of the solution. If chlorides are present, the chromium dioxydichloride rises instantly as a bright brownish-red gas. The *distinction from bromine* requires, however, that the material, which should be dry, should be *distilled*, by means of a tubulated flask or small retort, the vapors being condensed in a receiver, and neutralized with an alkali (*c* and *d*). The chromate formed makes a yellow solution (bromine, a colorless solution). As conclusive evidence of chlorine, the chromate (acidified with acetic acid), with lead acetate, forms a yellow precipitate (bromide, a white precipitate, if any):

(*c*) $CrO_2Cl_2 + 2H_2O = H_2CrO_4 + 2HCl$

(*d*) $CrO_2Cl_2 + 4(NH_4)OH = (NH_4)_2CrO_4 + 2NH_4Cl + 2H_2O$

(*e*) To detect a chloride in the presence of a cyanide or thiocyanate, add an excess of silver nitrate, filter and wash. To the moist precipitate add a few drops of silver nitrate (§318, 21) and then several cubic centimeters of concentrated sulphuric acid and boil for two or three minutes. The silver cyanide and thiocyanate are completely dissolved with decomposition, while the silver chloride is not changed except on *long continued boiling*. The student should confirm by tests on known material.

According to Borchers (*C. N.*, 1883, **47**, 218), to detect a chloride in the presence of a cyanide or a thiocyanate add silver nitrate, filter, wash, and boil the precipitate with concentrated nitric acid to complete oxidation of the cyanogen compound. See Mann (*Z.*, 1889, **28**, 668) for detection of a chloride in presence of an alkali thiocyanate by use of $CuSO_4$ and H_2S.

(*f*) If a solution containing iodides, bromides, and chlorides be boiled with $Fe_2(SO_4)_3$, all the iodine is liberated and may be collected in a solution of **KI** and estimated with standard $Na_2S_2O_3$. The solution should

* With the chlorides of mercury no brown fumes are obtained as these chlorides are not transposed by the sulphuric acid; and the chlorides of lead, silver, antimony, and tin are so slowly transposed that the formation of the chromium dioxydichloride may escape observation. Before relying upon this test the absence of the above named metals should be assured.

be cooled to about 60° and a slight excess of $KMnO_4$ added. The bromine is all liberated and may be collected in NH_4OH and estimated as a bromide after reduction with SO_2. The chloride may now be detected in the filtrate and may be estimated by one of the usual methods. Aspiration aids the removal of the iodine and bromine (Weiss, *C. C.*, 1885, 634 and 712; Hart, *C. N.*, 1884, **50**, 268).

(*g*) Villiers and Fayotte (*C. r.*, 1894, **118**, 1152, 1204 and 1413) detect a chloride in presence of an iodide and bromide by passing the liberated halogens into a solution of aniline in acetic acid (400 cc. of a saturated water solution of aniline to 100 cc. of glacial acetic acid) use 3 to 5 cc. of this solution for each test. Iodine gives no precipitate; bromine gives a white precipitate; and chlorine a black precipitate. If the bromide be present in large excess, add silver nitrate, digest the precipitate with ammonium hydroxide, add hydrogen sulphide and test the filtrate as the original solution. Liberate the halogen with $KMnO_4$ and H_2SO_4.

(*h*) Deniges (*Bl.*, 1890, (3), **4**, 481; 1891, (3), **5**, 66) uses H_2SO_4 and Fe''' to liberate the iodine, and K_2CrO_4 to liberate the bromine; then after boiling off the I and Br he adds $KMnO_4$ to liberate the chlorine. The iodine he detects with starch paper, the bromine fumes are absorbed on a rod moistened with KOH, which then gives an orange-yellow color with aniline. The chlorine he collects as the bromine and obtains a violet color with aniline.

(*i*) Dechan (*J. C.*, 1886, **50**, 682; 1887, **51**, 690) removes iodine of iodides by distilling with a concentrated solution of $K_2Cr_2O_7$; then the bromine of bromides by adding dilute H_2SO_4 and again distilling. The chloride is precipitated by $AgNO_3$ after dilution and addition of HNO_3.

(*j*) Vortman (*M.*, 1882, **3**, 510; *Z.*, 1886, **25**, 172) detects chlorine in presence of bromine and iodine as follows: The solution containing the halogens combined with the alkali or alkaline earth metals is heated with acetic acid and peroxide of lead until the supernatant liquid is colorless and has no longer the slightest odor of iodine or bromine; in this way the whole of the bromine and part of the iodine are driven off, the remainder of the latter remaining as iodate of lead along with the excess of lead peroxide. This is filtered off, the precipitate washed with boiling water, and the chlorine precipitated from the filtrate by addition of silver nitrate.

(*k*) The halogens may also be very readily separated by means of potassium persulphate, $K_2S_2O_8$ (§318, 15). In dilute acetic acid iodine is liberated while bromides and chlorides are not oxidized. On acidifying with H_2SO_4 bromine is liberated, while there is no action on chlorides if the strength of the sulphuric acid does not exceed 2N. If the free iodine and bromine have been removed by CS_2 or boiling, the chlorine may be

precipitated by means of $AgNO_3$. As in the presence of chlorates the iodine is oxidized to IO_3, ClO_3 must be absent. If present, the halogens must be precipitated as silver salts and reduced with metallic zinc.

The following reactions take place:

$$2KI + K_2S_2O_8 = 2K_2SO_4 + I_2.$$

$$2KBr + K_2S_2O_8 + H_2SO_4 = 2K_2SO_4 + Br_2 + H_2SO_4.$$

$$KCl + K_2S_2O_8 + H_2SO_4(1.5—2N) = \text{No action.}$$

$$2AgI + 2AgBr + 2AgCl + 3Zn = 6Ag + ZnI_2 + ZnBr_2 + ZnCl_2.$$

9. **Estimation.**—(*a*)—It is precipitated by $AgNO_3$, washed, and after ignition, weighed as $AgCl$. (*b*) By a standard solution of $AgNO_3$. A little Na_2HPO_4, or, better, $K_2Cr_2O_7$, is added to the chloride to show the end of the reaction. When enough $AgNO_3$ has been added to combine with the chlorine the next addition gives a yellow precipitate with the phosphate, or a red with the chromate.

§270. Hypochlorous acid. $HClO = 52.468$.

$H'Cl'O^{—''}$, $H — O — Cl$.

1. **Properties.**—Hypochlorous anhydride, Cl_2O, is a reddish-yellow gas, condensing at about —20° to a blood-red liquid, which boils at about —17° (Pelouze, *A. Ch.*, 1843, (3), **7**, 176). Rise of temperature causes decomposition, explosively, into chlorine and oxygen (Balard, *A. Ch.*, 1834, **57**, 225). *Molecular weight*, 86.9. *Vapor density*, 43.5 at 10°. The acid, $HClO$, has not been isolated. Its aqueous solution smells like Cl_2O, decomposing rapidly, especially in the sunlight, into Cl and $HClO_3$.

2. **Occurrence.**—Not found in nature.

3. **Formation.**—(*a*) By adding chlorine to HgO in the presence of water: $2HgO + 2Cl_2 + H_2O = Hg_2OCl_2 + 2HClO$ (Carius, *A.*, 1863, **126**, 196). (*b*) By adding five per cent nitric acid to calcium hypochlorite and distilling at a low temperature (Koffer, *A.*, 1875, **177**, 314). (*c*) By passing chlorine into the sulphates of Mg, Zn, Al, Cu, Ca or Na: $Na_2SO_4 + Cl_2 + H_2O = NaHSO_4 + NaCl + HClO$. (*d*) By heating a mixture of $KClO_3$ and $H_2C_2O_4$ to 70° (Calvert and Davies, *A. Ch.*, 1859, (3), **55**, 485).

4. **Preparation.**—For commercial purposes, as a bleaching agent and as a disinfectant; used as calcium hypochlorite with calcium chloride, chlorinated lime, made by bringing chlorine in contact with calcium hydroxide, without heating. Lunge and Schoch (*B.*, 1887, **20**, 1474) give the formula $Ca\begin{matrix}—OCl\\—Cl\end{matrix}$ to chlorinated lime. See also Kraut (*A.*, 1882, **214**, 244). Also as sodium hypochlorite, made by treating sodium hydroxide with chlorine short of saturation in the cold: $2NaOH + Cl_2 = NaClO + NaCl + H_2O$. The sodium hypochlorite-and-chloride mixed as formed by chlorine in solution of sodium hydroxide or sodium carbonate, or by double decomposition between solution of the calcium hypochlorite-and-chloride and solution of sodium carbonate—is pharmacopœial, under the name of solution of chlorinated soda ($NaCl.NaClO$).

5. **Solubilities.**—Hypochlorites are all soluble in water and are decomposed by heating.

6. **Reactions.**—The hypochlorites are all unstable. They are decomposed by nearly all acids, including CO_2: $2Ca(ClO)_2 + 2CO_2 = 2CaCO_3 + 2Cl_2 + O_2$;

$4NaClO + 4HCl = 4NaCl + 2H_2O + 2Cl_2 + O_2$. They are very powerful oxidizing agents, acting in acid solution as free chlorine, as the above equations indicate. Hypochlorites act as chlorine in alkaline mixture (§268, 6) (Fresenius, *Z. angew.*, 1895, 501). On warming, all hypochlorites when in solution are converted into chlorides and chlorates:

$$3NaClO = 2NaCl + NaClO_3.$$

In the presence of 40 per cent or more of caustic potash, potassium hypochlorite decomposes into chloride with evolution of oxygen (Winteler, *Z. angew.*, **33**, (1902), 778).

When shaken with mercury, hypochlorites or free hypochlorous acid produce a reddish basic mercuric chloride, insoluble in water, soluble in **HCl** (distinction from free chlorine, which produces white mercurous chloride insoluble in **HCl**).

7. **Ignition.**—All hypochlorites are decomposed by heat: $2KClO = 2KCl + O_2$.

8. **Detection.**—Although silver hypochlorite is soluble in water, it decomposes very quickly, so that on adding silver nitrate to sodium hypochlorite the final reaction is as follows: $3NaClO + 3AgNO_3 = 2AgCl + AgClO_3 + 3NaNO_3$. When **KClO** is shaken with **Hg**°, yellowish-red Hg_2OCl_2 is formed; the other potassium salts of chlorine, *i. e.*, **KCl**, $KClO_2$, $KClO_3$ and $KClO_4$, have no action upon **Hg**°. An indigo solution is decolored by hypochlorites, while $KMnO_4$ is not decolored. If arsenous acid be present, the indigo solution is not decolored until the arsenous acid is all oxidized to arsenic acid.

9. **Estimation.**—It is estimated as **AgCl** after reduction with **Zn** and H_2SO_4. Rosenbaum (*Z. angew.*, 1893, 80) gives a method for estimating the various chlorine compounds in chlorinated lime.

§271. Chlorous acid. $HClO_2 = 68.468$.

$$H'Cl'''O^{-''}{}_2, \quad H-O-Cl=O.$$

1. **Properties.**—The anhydride, Cl_2O_3, has not been isolated and the free acid is known only in solution, and this generally contains some $HClO_3$. It has an intense yellow color and is very unstable.

2. **Occurrence.**—Neither the acid nor its salts are found in nature.

3. **Formation.**—An impure chlorous acid is said to be formed when $KClO_3$ is treated with HNO_3 and As_2O_3, $C_{12}H_{22}O_{11}$ or C_6H_6 (Millon, *A. Ch.*, 1843, (3), **7**, 298; Schiel, *A.*, 1859, **109**, 318; Carius, *A.*, 1866, **140**, 317). Chlorites of a number of metals have been made by adding the bases to a water solution of the acid; also from $KClO_2$ by transposition.

4. **Preparation.**—$KClO_2$ is prepared by adding an aqueous solution of ClO_2 of known strength to the proper quantity of **KOH**, and evaporating in a vacuum. The crystals of $KClO_3$ which are formed in the reaction are removed and the mother liquor is crystallized from alcohol.

5. **Solubilities.**—All chlorites which have been prepared are soluble in water, lead and silver chlorites sparingly soluble.

6. **Reactions.**—Chlorous acid or potassium chlorite in dilute acid solution is a powerful oxidizing agent, acting similar to chlorine.

7. **Ignition.**—Chlorites when heated evolve oxygen and leave a chloride, or first a chloride and a chlorate (Brandau, *A.*, 1869, **151**, 340).

8. **Detection.**—A concentrated solution of a chlorite gives a white precipitate with silver nitrate, fairly readily soluble in more water. $KMnO_4$ is decolored, a brown precipitate being formed. A solution of indigo is decolored even in presence of arsenous acid (distinction from hypochlorous acid). Chlorites when slightly acidulated give a transient amethyst tint to a solution of ferrous sulphate.

9. **Estimation.**—By reduction to chloride and estimation as such. By meas-

uring the amount of ferrous iron oxidized to the ferric condition: $4FeSO_4 + HClO_2 + 2H_2SO_4 = 2Fe_2(SO_4)_3 + HCl + 2H_2O$.

§272. Chlorine Peroxide. $ClO_2 = 67.46$.

$$Cl^{IV}O^{-''}{}_2, \begin{matrix} O = \\ O = \end{matrix} Cl - O - Cl = O \text{ or } O = Cl = O\ *.$$

Chlorine peroxide, ClO_2, at ordinary temperature, is a dark greenish-yellow gas. In concentrated solution it has very much the odor of nitrous acid. Cooled in a mixture of ice and salt it condenses to a bromine-red liquid; and in a mixture of solid CO_2 and ether it forms a mass of orange-yellow, brittle crystals. When warmed to about 60° it explodes with violence. In direct sunlight at ordinary temperature it decomposes slowly into chlorine and oxygen, while in the dark it is quite stable. In contact with many substances, as phosphorus, sulphur, sugar, ether, turpentine, etc., it explodes at ordinary temperature. In moist condition it bleaches blue litmus-paper without previously reddening it.

One volume of water absorbs about 20 volumes of the gas at 4° (Millon, *A. Ch.*, 1843, (3), **7**, 298). The solution in water contains $HClO_2$ and $HClO_3$.

It is prepared by carefully adding $KClO_3$ to cold concentrated H_2SO_4; the mixture is then carefully warmed to 20°, later somewhat higher. The gas is condensed in a tube cooled by a mixture of ice and salt: $3KClO_3 + 2H_2SO_4 = 2KHSO_4 + KClO_4 + H_2O + 2ClO_2$ (Millon, *l. c.*). It is also made by warming a mixture of oxalic acid and potassium chlorate. When prepared in this manner it is mixed with CO_2: $2KClO_3 + 2H_2C_2O_4 = K_2C_2O_4 + 2H_2O + 2ClO_2 + 2CO_2$ (Calvert and Davies, *A.*, 1859, **110**, 344). It is also formed, mixed with chlorine, when $KClO_3$ is warmed with HCl. HI is oxidized to I; SO_2 to H_2SO_4. Indigo is bleached even in presence of As_2O_3.

§273. Chloric acid. $HClO_3 = 84.468$.

$$H'Cl^{V}O^{-''}{}_3, H - O - Cl \begin{matrix} = O \\ = O \end{matrix}$$

1. **Properties.**—A solution of chloric acid may be evaporated in a vacuum until its *specific gravity* is 1.282 at 14°. The composition is then $HClO_3.7H_2O$, containing 40.1 per cent $HClO_3$ (Kaemmerer, *Pogg.*, 1869, **138**, 390). Farther attempts at concentration on heating to 40° result in evolution of chlorine and oxygen, forming $HClO_4$: $8HClO_3 = 4HClO_4 + 2H_2O + 3O_2 + 2Cl_2$ (Serullas, *A. Ch.*, 1830, **45**, 270). Its solution in the cold is odorless and colorless; first reddening and then bleaching litmus. It is a strong oxidizing agent, paper soaked with the acid takes fire on drying. The anhydride, Cl_2O_5, has not been isolated.

2. **Occurrence.**—Does not occur in nature.

3. **Formation.**—The free acid may be formed by adding an excess of H_2SiF_6 to a hot solution of $KClO_3$; the filtrate is evaporated in vacuo, the excess of H_2SiF_6 volatilizes, leaving the $HClO_3$. Many chlorates are formed by treating the metallic hydroxides with the free acid. Also by the action of $Ba(ClO_3)_2$ upon the sulphate of the metal whose chlorate is required; or by the action of the chloride of the chlorate needed, upon a solution of $AgClO_3$.

* Pebal, *A.*, 1875, 177, 1.

4. **Preparation.**—By adding H_2SO_4 in molecular proportions to a solution of $Ba(ClO_3)_2$. Chlorates of the fifth and sixth group metals are prepared by passing chlorine into the respective hydroxides dissolved or suspended in water. By repeated crystallization the chlorate is separated from the chloride which is also formed: $6KOH + 3Cl_2 = 5KCl + KClO_3 + 3H_2O$.

5. **Solubilities.**—All chlorates are soluble in water, the chlorates of **Hg**, **Sn**, and **Bi** require a little free acid. Mercurous and ferrous chlorates are very unstable. Potassium chlorate is the least soluble of the stable metallic chlorates; soluble in about 21 parts water at 10° (Blarez, *C. r.*, 1891, **112**, 1213).

6. **Reactions.** *A.*—**With metals and their compounds.**—Chloric acid attacks **Mg** evolving hydrogen and forming a chlorate only. With **Zn**, **Fe**, **Sn**, and **Cu** some chloride is also formed. With **Zn** and H_2SO_4 the reduction to chloride is complete, and with sodium amalgam no reduction whatever (Thorpe, *J. C.*, 1873, **26**, 541). With the zinc-copper couple * the reduction to a chloride is rapid and complete. The hot concentrated acid attacks all metals. With oxides or hydroxides the acid forms chlorates provided a chlorate of that metal can by any means be formed. Free chloric acid is a strong oxidizing agent, and if an excess of the reducing agent is used, it is converted into hydrochloric acid, or a chloride. With the aid of heat the chloric acid splits up, forming some chlorine and oxides of chlorine.

Hg' forms Hg''.

As''' forms As^{V}.

Sb''' forms Sb^{V}.

Sn'' forms Sn^{IV}.

Cu' forms Cu''.

Cr''' forms Cr^{VI}, chromic salts are readily oxidized to chromic acid on boiling with $KClO_3$ and HNO_3.

Fe'' forms Fe''' (a distinction from perchloric acid) (Carnot, *C. r.*, 1896, **122**, 452).

Mn'' forms Mn^{IV}, manganous salts are rapidly oxidized to MnO_2 on warming with $KClO_3$ and HNO_3.

Salts of lead, cobalt, and nickel do not appear to be oxidized on boiling with $KClO_3$ and HNO_3.

B.—**With non-metals and their compounds.**

1. $H_2C_2O_4$ forms CO_2 and varying proportions of **Cl** and **HCl**. Heat and excess of oxalic acid favors the production of **HCl** (Guyard, *Bl.*, 1879,

* Gladstone and Tribe's copper-zinc couple is prepared by treating thin zinc foil with a 1 per cent solution of copper sulphate until the zinc is covered with a black deposit of reduced copper. When washed and dried it is ready for use.

(2), **31**, 299). All oxalates are decomposed, CO_2 and a chlorate or chloride of the metal being formed. Carbonates are all transposed.

HCNS forms H_2SO_4, **HCN**, and **HCl**.

$H_4Fe(CN)_6$ first forms $H_3Fe(CN)_6$ and **HCl**; a great excess of $HClO_3$ decomposes the $H_3Fe(CN)_6$.

2. HNO_2 forms HNO_3 and **Cl**. Nitrites are transposed and oxidized, forming chlorates or nitrates of the metal.

3. PH_3, HH_2PO_2, and H_3PO_3 form H_3PO_4 and **HCl**. Hypophosphites and phosphites are transposed and then oxidized, H_3PO_4 and a chlorate or a chloride of the metal being produced.

4. S^{VI-n} forms S^{VI} and **HCl**; that is, the sulphur of all compounds becomes H_2SO_4 with formation of **HCl**. All sulphides, sulphites, thiosulphates, etc., are transposed, forming a chlorate, chloride, or sulphate of the metal.

5. **HCl** in excess forms only **Cl** and H_2O (§**269**, *6B5*). **NaCl** warmed with $HClO_3$ evolves **Cl**, leaving only $NaClO_3$.

6. **HBr** forms **Br** and **HCl**. **KBr** warmed with $HClO_3$ evolves **Br**, leaving only $KClO_3$.

7. **I** and **HI** form HIO_3 and **HCl**. Soluble iodides form iodic acid or an iodate.

7. **Ignition.**—All chlorates are resolved by heat into chlorides and oxygen: $2KClO_3 = 2KCl + 3O_2$. Some perchlorate is usually formed as an intermediate product: $2KClO_3 = KClO_4 + KCl + O_2$ (Serullas, *A. Ch.*, 1830, (2), **45**, 270). In presence of various metallic oxides, etc., the oxygen is separated more easily, the metallic oxides remaining unchanged. With manganese dioxide, the oxygen of potassium chlorate is obtained at about 200°; ferric oxide, platinum black, copper oxide, and lead dioxide may be used (§**242**, 3). If chlorates are rapidly ignited some chlorine is given off (Spring and Prost, *Bl.*, 1889, (3), **1**, 340). When *triturated or heated* with **combustible substances**, charcoal, organic substances, sulphur, sulphites, cyanides, thiosulphates, hypophosphites, reduced iron, etc.—*chlorates violently explode*, owing to their sudden decomposition, and the simultaneous oxidation of the combustible material. This explosion is more violent than with corresponding mixtures of nitrates.

Alkali chlorates when **fused with an alkali**, or an alkali carbonate, and a free metal or a lower oxide, or salt of the metal, generally oxidizes it to a higher oxide, or to a salt having an increased number of bonds; and the chlorate is reduced to a chloride—*e. g.*, Mn^{VI-n} becomes Mn^{VI}. That is, any compound of manganese having less than six bonds is oxidized to the hexad (*a*). Cr''' becomes Cr^{VI} (*b*). As^{V-n} becomes As^{V} (*c*). Pb^{IV-n}

becomes Pb^{IV} (*d*). Co'''^{-n} becomes Co''' (*e*). C^{IV-n} becomes C^{IV} (*f*). P^{V-n} becomes P^{V} (*g*). I^{V-n} becomes I^{V} (*h*). S^{VI-n} becomes S^{VI} (*i*).

(*a*) $3Mn_3O_4 + 18KOH + 5KClO_3 = 9K_2MnO_4 + 5KCl + 9H_2O$
(*b*) $2CrCl_3 + 10NaOH + NaClO_3 = 2Na_2CrO_4 + 7NaCl + 5H_2O$
(*c*) $3As_4 + 36KOH + 10KClO_3 = 12K_3AsO_4 + 10KCl + 18H_2O$
(*d*) $3Pb_3O_4 + Na_2CO_3 + 2NaClO_3 = 9PbO_2 + 2NaCl + Na_2CO_3$
(*e*) $6CoCl_2 + 12KOH + KClO_3 = 3Co_2O_3 + 13KCl + 6H_2O$
(*f*) $3K_2C_4H_4O_6 + 5KClO_3 = 5KCl + 3K_2CO_3 + 9CO_2 + 6H_2O$
(*g*) $3Pb(H_2PO_2)_2 + 18KOH + 5KClO_3 = 3PbO_2 + 6K_3PO_4 + 5KCl + 15H_2O$
(*h*) $ZnI_2 + K_2CO_3 + 2KClO_3 = ZnO + 2KIO_3 + 2KCl + CO_2$
(*i*) $3K_2S_5O_6 + 12K_2CO_3 + 10KClO_3 = 15K_2SO_4 + 10KCl + 12CO_2$

8. **Detection.** (*a*) Dry chlorates when warmed with concentrated sulphuric acid, detonate evolving yellow fumes: $3KClO_3 + 2H_2SO_4 = 2KHSO_4 + KClO_4 + 2ClO_2 + H_2O$. This action is modified by reducing agents; some acting rapidly, increase the detonation; others acting slowly, lessen it. (*b*) $HClO_3$, like HNO_3, decolors indigo solution and gives colors with brucine, diphenylamine, paratoluidine, and phenol similar to those formed by HNO_3. (*c*) By ignition a chloride is left: $2KClO_3 = 2KCl + 3O_2$. (*d*) It is changed to a chloride by nascent hydrogen: $2KClO_3 + 6Zn + 7H_2SO_4 = 6ZnSO_4 + K_2SO_4 + 2HCl + 6H_2O$; or by reducing acids or bases: $2KClO_3 + H_2SO_4 + 6H_2SO_3 = K_2SO_4 + 6H_2SO_4 + 2HCl$. The resulting HCl is then identified in the usual manner. Chlorides, if originally present, should first be removed by silver nitrate.

9. **Estimation.**—(*a*) Reduction to a chloride and estimation as such. (*b*) Addition of HCl and KI and estimation of the liberated iodine with standard $Na_2S_2O_3$.

§274. Perchloric acid. $HClO_4 = 100.468$.

$$= 0$$
$$H'Cl^{VII}O^{-''}_4;\ H-O-Cl = 0$$
$$= 0$$

1. **Properties.**—*Specific gravity*, 1.782 at 15°. The anhydrous $HClO_4$ is a colorless oily liquid, volatile but cannot be distilled without partial decomposition, often with explosive violence. Only its solution in water can be safely handled. Paper, charcoal, ether, phosphorus, and many other substances when brought in contact with the anhydrous acid take fire. The dilute acid is very stable, not being easily reduced (Berthelot, *A. Ch.*, 1882, (5), **27**, 214). It does not bleach, but merely reddens blue litmus paper.

2. **Occurrence.**—Not found in nature.

3. **Formation.**—(*a*) By electrolysis of a solution of Cl or HCl in water (Riche, *C. r.*, 1858, **46**, 348). (*b*) $KClO_4$ is formed by electrolysis of $KClO_3$, using platinum electrodes (Lidoff and Tichomiroff, *J. C.*, 1883, **44**, 149). (*c*) $KClO_3$ is heated with an excess of H_2SiF_6, after cooling and filtering, the filtrate is carefully distilled (Roscoe, *J. C.*, 1863, **16**, 82; *A.*, 1862, **121**, 346). (*d*) By treating the sulphate of the metal, the perchlorate of which is desired,

with $Ba(ClO_4)_2$ in molecular proportions. (*e*) By treating the chloride of the metal, the perchlorate of which is desired, with $AgClO_4$ in molecular proportions.

4. **Preparation.**—$KClO_4$ is made by carefully heating $KClO_3$ until no more oxygen is evolved: $2KClO_3 = KCl + KClO_4 + O_2$ (7). The residue is dissolved in water and upon cooling crystals of $KClO_4$ separate. The free acid, nearly pure, is obtained by cautiously distilling $KClO_4$ with concentrated H_2SO_4.

5. **Solubilities.**—All of the perchlorates of the ordinary metals are soluble in water, and all are deliquescent except NH_4ClO_4, $KClO_4$, $Pb(ClO_4)_2$ and $HgClO_4$ (Serullas, *A. Ch.*, 1831, **46**, 362). Potassium perchlorate is soluble in 142.9 parts of water at 0°, in 52.5 parts at 25°, and in 5 parts at 100° (Muir, *C. N.*, 1876, **33**, 15). $KClO_4$ is insoluble in alcohol (distinction from $NaClO_4$) (Schloessing, *A. Ch.*, 1877, (5), **11**, 561).

6. **Reactions.**—Iron and zinc evolve hydrogen when treated with perchloric acid. The acid reacts with the hydroxides of many metals to form perchlorates. It is not reduced by HCl, HNO_3, H_2S or SO_2. Iodine is oxidized to HIO_4 with liberation of chlorine: $I_2 + 2HClO_4 = 2HIO_4 + Cl_2$. A solution of indigo is not decolored by $HClO_4$ even after the addition of HCl (distinction from all other oxyacids of chlorine). It is not reduced by the zinc-copper couple (distinction from chlorate). Sodium perchlorate, $NaClO_4$, is used as a reagent to precipitate potassium salts.

7. **Ignition.**—Perchlorates strongly ignited evolve oxygen and leave a chloride (§242, 3).

8. **Detection.**—In presence of a hypochlorite, chlorite, chlorate and chloride boil thoroughly with HCl; the first three are decomposed, leaving chloride and perchlorate. Remove the chloride with $AgNO_3$ and fuse the evaporated filtrate with Na_2CO_3. Dissolve the fused mass in water and test for a chloride; its presence indicates the previous presence of a perchlorate. Perchlorates may also be separated from the other chlorine acids by passing SO_2 gas, which reduces all the chlorine acids excepting perchloric acid. Blattner & Brasseur, *Ch. Z.*, **24**, 793.

9. **Estimation.**—(*a*) After being changed to a chloride as indicated above, it is estimated in the usual manner. (*b*) It is fused with zinc chloride and the amount of chlorine liberated measured by the amount of iodine set free from a solution of potassium iodide (separation from chlorate, chlorides and nitrates). (*c*) $KClO_4$ is heated to 200° with HPO_3 and KI; the iodine liberated showing the amount of perchlorate present (Gooch and Kreider, *Am. S.*, 1894, **48**, 33; and 1895, **49**, 287).

§275. Bromine. Br = 79.92. Valence one and five.

1. **Properties.**—*Molecular weight*, 159.8; *vapor density*, 80; *specific gravity*, 3.18828 at 0°; *boiling point*, 58.7°. At −7.3° it becomes a brown solid (Burgess, *Wash. Acad. of Sc.*, 1 18). At ordinary temperatures **bromine** is a brown-red, intensely caustic liquid, freely evolving brown vapors, corrosive vapors of a suffocating chlorine-like odor. As a solid it is still darker in color. It reacts with KOH in all respects similar to chlorine (§268, 1). Indigo, litmus and most other organic coloring matters are bleached. A solution of starch is colored slightly yellow.

Bromine decomposes hydrosulphuric acid with separation of sulphur, and subsequent production of sulphuric acid; changes ferrous to ferric salts, and (in presence of water) acts as a strong oxidizing agent. It displaces iodine from iodides, and is displaced from bromides by chlorine; its character being intermediate between that of chlorine and that of iodine.

No oxides of bromine have, with certainty, been isolated. The well-established acids are: Hydrobromic, **HBr**; hypobromous, **HBrO**; bromic, $HBrO_3$.

2. **Occurrence.**—Not found free in nature. As a bromide in sea water, mother liquor from salt wells, mineral springs, and in a few minerals.

3. **Formation.**—(*a*) Hydrobromic acid or any soluble bromide is warmed with MnO_2 and H_2SO_4. (*b*) Any soluble bromide is treated with chlorine water and the solution warmed.

4. **Preparation.**—The bromine of commerce is obtained chiefly from the mother liquor of the salt works: (*a*) By treating with MnO_2 and H_2SO_4: $MgBr_2 + MnO_2 + 2H_2SO_4 = MgSO_4 + MnSO_4 + Br_2 + 2H_2O$. (*b*) By leading a current of steam and chlorine into the bottom of a vessel filled with coke, into which a stream of the mother liquor flows from above: $MgBr_2 + Cl_2 = MgCl_2 + Br_2$. (*c*) By adding to the mother liquor a mixture of $Mg(OH)_2$, suspended in water and saturated with chlorine, rendering acid and distilling in a current of steam: $Mg(ClO_3)_2 + 6MgBr_2 + 12HCl = 7MgCl_2 + 6H_2O + 6Br_2$. (*d*) By electrolysis of the mother liquor at a low temperature and then distilling in a current of steam.

Commercial bromine is freed from chlorine by adding **KBr** and distilling. If iodine be present it is first removed as **CuI**.

5. **Solubilities.**—Bromine dissolves in 30 parts of water at 15°, forming an orange-yellow solution (Dancer, *J. C.*, 1862, **15**, 477). Its water solution is not permanent, but slowly decomposes: $2Br_2 + 2H_2O = 4HBr + O_2$. Much more soluble in **HCl**, **HBr**, **Kbr**, $BaCl_2$, $SrCl_2$, and in many other salts than in water. Soluble in carbon disulphide, chloroform, ether and alcohol. Readily removed from its solution in water by shaking with carbon disulphide or chloroform, imparting a brown color to the solvent.

6. **Reactions.** *A.*—**With metals and their compounds.**—Bromine unites directly with gold, platinum, and all ordinary metals to form bromides. It combines with metallic mercury forming the insoluble mercurous bromide. Silver salts are precipitated, yellow-white, as bromide and bromate: $6AgNO_3 + 3Br_2 + 3H_2O = 5AgBr + AgBrO_3 + 6HNO_3$. In the following metallic compounds the valence of the metal is changed; the bromine being reduced to **HBr** or, if in alkaline mixture, to a bromide. The reaction is less violent than with chlorine.

1. **Pb″** becomes PbO_2 in alkaline mixture only.

2. **Hg′** becomes **Hg″** in acid and in alkaline mixture.

3. **As‴** becomes As^V in acid and in alkaline mixture. With AsH_3 and a solution of bromine in water H_3AsO_3 is first formed, and if the bromine be in excess the final products are H_3AsO_4 and **HBr**.

4. **Sb‴** becomes Sb^V in acid and in alkaline mixture.

5. **Sn″** becomes Sn^{IV} in acid and in alkaline mixture.

6. **Bi‴** becomes Bi_2O_5 in alkaline mixture only.

7. **Cu′** becomes **Cu″** in acid and alkaline mixture.

8. **Cr‴** becomes Cr^{VI} in alkaline mixture only.

9. **Fe″** becomes **Fe‴** in acid mixture; in alkaline mixture the iron is further oxidized to a ferrate, **HBr** or a bromide being formed.

10. **Co″** becomes **Co‴** in alkaline mixture only.

11. **Ni″** becomes **Ni‴** in alkaline mixture only (Kilpius, *J. C.*, 1876, **29**, 742).

12. Mn^{IV-n} becomes Mn^{IV} in alkaline mixture only.

B.—**With non-metals and their compounds.**

1. $H_2C_2O_4$ becomes a carbonate and a bromide in alkaline mixture. An excess of hot saturated oxalic solution changes **Br** to **HBr**.

HCNS forms, among other products, H_2SO_4 and a bromide in acid mixture, and a sulphate and a bromide in alkaline mixture.

$H_4Fe(CN)_6$ in acid mixture forms $H_3Fe(CN)_6$ and **HBr**, in alkaline mixture a ferricyanide and a bromide (Wagner, *J. C.*, 1876, **29**, 741).

2. HNO_2 becomes HNO_3 and **HBr** if dilute and cold.

3. PH_3, HH_2PO_2 and H_3PO_3 become H_3PO_4 and **HBr** with acids, and a phosphate and a bromide in alkaline mixture. **P** and **Br** unite to form PBr_3 or PBr_5, depending upon relative amounts of the elements present. The phosphorus bromides are decomposed by water, forming **HBr** and the corresponding acids of phosphorus.

4. S°, H_2S, H_2SO_3, $H_2S_2O_3$, S^{VI-n} becomes H_2SO_4 and **HBr** with acids, a sulphate and a bromide in alkaline mixture.

5. **Br** does not act as an oxidizing agent upon the compounds of chlorine, but may, at low temperatures, combine with chlorine to form a chlorine bromide, **BrCl** (Bornemann, *A.*, 1877, 189, 183).

6. In alkaline mixture **hypobromites** by boiling are oxidized to bromates with formation of a bromide.

7. **Iodine** becomes an iodate and a bromide in alkaline mixture; the elements may combine to form the unstable bromiodide, **IBr** (Bornemann, *l. c.*). **HI** and iodides form **I** and **HBr**, but in alkaline mixture an iodate and a bromide are produced.

7. **Ignition.**—Warming drives off all the bromine from its solutions in water or other solvents. Heat favors all reactions with bromine.

8. **Detection.**—Bromine is usually detected by shaking its solution in water with CS_2, which dissolves it with a reddish-yellow color; if present in large quantities the color is brown to brownish black. In this case a large excess of CS_2 must be used or a very small portion of the unknown taken, in order that the solution be dilute enough for the reddish-yellow bromine color to be distinguished from the violet color of iodine. Ether or chloroform may be used instead of carbon disulphide, but the solution is of a paler yellow. Starch solution gives a yellow color with bromine, but the reaction is less delicate than with CS_2.

9. **Estimation.**—(*a*) The bromine is made to act upon **KI**, and the iodine which is liberated is estimated by standard solution of $Na_2S_2O_3$. (*b*) It is estimated by the amount of As_2O_3 which it oxidizes in alkaline solution. (*c*) It is converted into **HBr** by H_2S or H_2SO_3, and then precipitated by $AgNO_3$, and weighed as **AgBr**.

§276. Hydrobromic acid. HBr = 80.928.

H'Br⁻', H — Br.

1. **Properties.**—*Molecular weight*, 149.9. *Vapor density*, 39.1. A colorless gas, condenses to a liquid at —69° and solidifies at —73° (Faraday, *A.*, 1845, **56**, 155). Its aqueous solution is colorless and is not decomposed by exposure to the air. The *specific gravity* of the saturated solution at 0° is 1.78; containing 82.02 per cent **HBr**, or very nearly $HBr.H_2O$. If a saturated solution is boiled, chiefly **HBr** is given off, and if a dilute solution is boiled, chiefly H_2O is given off, until in both cases the remaining liquid contains 47.38 to 47.86 per cent of **HBr**, its *sp. gr.* 1.485, its boiling point constant at 126°, and its composition almost exactly $HBr.5H_2O$, which distils over unchanged. Its vapor density of 14.1 agrees with the calculated vapor density of $HBr.5H_2O$.

2. **Occurrence.**—Not found free in nature, in combination as bromides in sea water and in some minerals.

3. **Formation.**—(*a*) By action of bromine upon phosphorus immersed in water, the amorphous phosphorus is preferred: $P_4 + 10Br_2 + 16H_2O = 4H_3PO_4 + 20HBr$. (*b*) By action of H_3PO_4 or H_2SO_4 on **KBr** (Bertrand, *J. C.*, 1876, **29**, 877). (*c*) By transposition of $BaBr_2$ by cold dilute H_2SO_4 added in molecular proportions. (*d*) By passing a mixture of **Br** and **H** over platinum sponge. (*e*) By action of **Br** on H_3PO_2. (*f*) By adding **Br** to Na_2SO_3.

Metallic bromides are formed: (*1*) By direct union of the elements, but in a few cases heat is required to effect the combination. (*2*) By action of **HBr** upon the metallic oxides, hydroxides and carbonates. (*3*) Many bromides are formed by action of **HBr** on the free metal, *ous* salts and not *ic* being formed. (*4*) Bromides of the first group are best made by precipitation. (*5*) Bromides of **K**, **Na**, **Ba**, **Sr** and **Ca** are made by the action of bromine on their hydroxides and subsequent fusion:

$$6KOH + 3Br_2 = KBrO_3 + 5KBr + 3H_2O$$
$$2KBrO_3 \text{ (ignited)} = 2KBr + 3O_2$$

4. **Preparation.**—(*a*) H_2S is added to a solution of bromine in water until the yellow color disappears; the solution is then distilled. The first portion of the distillate is rejected if it contains H_2S, and the latter portion if it contains H_2SO_4 (Recoura, *C. r.*, 1890, **110**, 784). (*b*) H_2SO_4 is added to a concentrated solution of **KBr**; after twenty-four hours the greater portion of the $KHSO_4$ has crystallized out. The remaining liquor is then distilled. The product usually contains traces of H_2SO_4. (*c*) By passing bromine into hot paraffine (Crismer, *B.*, 1884, **17**, 649).

5. **Solubilities.**—Silver and mercurous bromide are insoluble in water, lead bromide is sparingly soluble; all other bromides are soluble. Hydrobromic acid and soluble bromides precipitate solutions of the metals of the first group, lead salts incompletely. Lead bromide is less soluble than the corresponding chloride. The presence of soluble bromides increases the solubility of lead bromide. A small amount of hydrobromic acid decreases its solubility, but a larger excess increases it (Ditte, *C. r.*, 1881, **92**, 718).

In *alcohol*, the alkali bromides are sparingly or slightly soluble: calcium bromide, soluble; mercuric bromide, soluble; mercurous bromide, insoluble. **Silver bromide** is soluble in NH_4OH.

6. **Reactions.**—*A.*—**With metals and their compounds.**—Hydrobromic acid dissolves many metals with the formation of bromides and evolution of hydrogen, *e. g.*, **Pb**, **Sn**, **Fe**, **Al**, **Co**, **Ni**, **Zn**, and the metals of the

calcium and the alkali groups. It unites with salt forming oxides and hydroxides to produce bromides without change of valence: $PbO + 2HBr = PbBr_2 + H_2O$. But if the valence of the metal in the oxide or hydroxide is such that no corresponding bromide can be formed, then reduction takes place as follows:

1. Pb''^{+n} becomes $PbBr_2$ and **Br**.

2. As^V becomes As''' and **Br**. The **HBr** must be concentrated and in excess, and the As^V compound merely moistened with water: $H_3AsO_4 + 2HBr = H_3AsO_3 + Br_2 + H_2O$. In presence of much water the reverse action takes place: $H_3AsO_3 + Br_2 + H_2O = H_3AsO_4 + 2HBr$.

3. Sb^V becomes Sb''' and **Br**.

4. Bi^V becomes $BiBr_3$ and **Br**.

5. Fe^{VI} becomes Fe''' and not Fe'', and **Br**.

6. Cr^{VI} becomes $CrBr_3$ and **Br** (a separation from a chloride if the solution be dilute) (Friedheim and Meyer, *Z. anorg.*, 1891, **1**, 407). **KBr** is not decomposed by a boiling concentrated solution of $K_2Cr_2O_7$ (separation from **KI**) (Dechan, *J. C.*, 1887, **51**, 690).

7. Co''^{+n} becomes $CoBr_2$ and **Br**.

8. Ni''^{+n} becomes $NiBr_2$ and **Br**.

9. Mn''^{+n} becomes $MnBr_2$ and **Br** (§**269**, 8; Jannasch and Aschoff, *Z. anorg.*, 1891, **1**, 144 and 245). $KMnO_4$ liberates all the bromine from **KBr** in presence of $CuSO_4$ (a separation of bromide from chloride (Baubigny and Rivals, *C. r.*, 1897, **124**, 859 and 954).

Silver nitrate solution precipitates, from solutions of bromides, *silver bromide*, **AgBr**, yellowish-white in the light, slowly becoming gray to black. The precipitate is insoluble in, and not decomposed by, nitric acid, soluble in concentrated aqueous ammonia, nearly insoluble in concentrated solution of ammonium carbonate, slightly soluble in excess of alkali bromides, soluble in solutions of alkali cyanides and thiosulphates. It is slowly decomposed by chlorine in the cold, rapidly when heated in a stream of chlorine.

Solution of **mercurous nitrate** precipitates *mercurous bromide*, **HgBr**, yellowish-white, soluble in excess of alkali bromides.

Solutions of **lead salts** precipitate, from solutions not very dilute, *lead bromide*, $PbBr_2$, white.

B.—**With non-metals and their compounds.**

1. $H_3Fe(CN)_6$ becomes $H_4Fe(CN)_6$ and **Br**. The **HBr** must be in excess and concentrated, also the ferricyanide should be merely moistened with water, as in the presence of much water the reverse action takes place: $2K_4Fe(CN)_6 + Br_2 = 2K_3Fe(CN)_6 + 2KBr$.

2. HNO_2, in dilute solutions, no action (distinction from **HI**) (Gooch and Ensign, *Am. S.*, 1890, **140**, 145 and 283).

HNO_3 becomes **NO** and **Br**.

3. **Phosphorus** compounds are not reduced.

4. H_2SO_4 becomes SO_2 and **Br**. Both acids must be concentrated and hot, otherwise the reverse action takes place: $SO_2 + Br_2 + 2H_2O = H_2SO_4 + 2HBr$. With H_2SO_4, *sp. gr.* 1.41, no bromine is set free even when solution is boiled (Feit and Kubierschky, *J. Pharm.*, 1891, (5), **24**, 159). The bromine of bromides is all liberated when warmed to 70° or 80° with ammonium persulphate (separation from a chloride) (Engel, *C. r.*, 1894, **118**, 1263).

5. Chlorine liberates bromine from all bromides, even from fused silver bromide (Nihoul, *Z. angew.*, 1891, 441).

$HClO_3$ becomes **HCl** and **Br**. If the $HClO_3$ be concentrated other products may appear.

6. **HBrO** liberates **Br** from both acids; the same with $HBrO_3$.

7. HIO_3 becomes **I** and **Br**.

8. Hydrogen peroxide liberates the bromine from hydrobromic acid at 100° (a distinction and separation from chloride). The bromine can best be removed by aspiration (Cavazzi, *Gazzetta*, 1883, **13**, 174).

7. **Ignition.**—Some bromides can be sublimed undecomposed in presence of air; *e. g.*, $AsBr_3$, $SbBr_3$, **HgBr** and $HgBr_2$. Some can be sublimed only by exclusion of air and moisture; *e. g.*, $AlBr_3$ and $NiBr_2$. Bromides of sodium and potassium are not changed by heat. Silver bromide melts undecomposed. Many bromides, however, are more or less decomposed when ignited in presence of air and moisture: $CuBr_2$ becomes **CuBr** and **Br**.

8. **Detection.**—Bromides are usually oxidized to free bromine, which is detected by its physical properties and by its color when dissolved in CS_2 (§**275**, 5). The oxidizing agent used to liberate the bromine varies according to the conditions. Chlorine is more commonly employed and acts when cold (*6B5*). A large excess of chlorine is to be avoided, as it decolorizes bromine solutions with formation of a chlorbromide. Nitric acid when dilute acts slowly unless hot. H_2SO_4, dilute, fails to oxidize the **HBr** even when hot; but when concentrated and hot is sometimes preferred. If chlorine be used, the mixture if alkaline must first be acidified; otherwise a colorless bromate will be formed, free bromine not being a visible intermediate step in the oxidation: $KBr + 6KOH + 3Cl_2 = KBrO_3 + 6KCl + 3H_2O$. **If an iodide be present:** (*a*) In absence of a chloride precipitate with silver nitrate, and digest the precipitate with NH_4OH, which will dissolve the **AgBr** and none of the **AgI**. The filtrate may be treated with H_2S, which precipitates the silver as Ag_2S, leaving the bromine in the filtrate as NH_4Br, which may be detected in the usual way. (*b*) To the acid mixture add chlorine water and carbon disulphide, shake and continue the addition of the chlorine water until the violet color of the iodine solution disappears, when the brown color due to the bromine may be observed: $2KI + 2KBr + 7Cl_2 + 6H_2O = 2HIO_3 + Br_2$

$+ 4KCl + 10HCl$. (*c*) To the solution from which the bases have been removed add a cold saturated solution of potassium chlorate and dilute sulphuric acid (one of acid to four of water); warm until the solution is of a pale straw color, or colorless if only iodides are present. It may be necessary to add more of the solution of potassium chlorate to complete the oxidation of the iodine. Dilute the solution with water, cool, and shake with carbon disulphide. See also §269, 8.

$$6KI + 6KBr + 2KClO_3 + 7H_2SO_4 = 3I_2 + 3Br_2 + 7K_2SO_4 + 2HCl + 6H_2O$$
$$6I_2 + xBr_2 + 10KClO_3 + 5H_2SO_4 + 6H_2O = 12HIO_3 + xBr_2 + 5K_2SO_4 + 10HCl$$

9. **Estimation.**—(*a*) It is converted into **AgBr**, and after gentle ignition weighed as such. (*b*) The bromide is oxidized to free bromine, which is passed into a solution of **KI** and the liberated iodine titrated with standard $Na_2S_2O_3$. (*c*) The bromide is oxidized to bromine, which is passed into an alkaline solution of arsenous acid. The excess of the arsenous acid is titrated with a standard solution of $KMnO_4$.

§277. Hypobromous acid. $HBrO = 96.928$.

$$H'Br'O^{-''}, \quad H - O - Br.$$

The **anhydride**, Br_2O, has not been isolated. The **acid**, $HBrO$, is a very unstable yellow liquid, a strong oxidizing and bleaching agent. The hypobromites are less stable than the corresponding hypochlorites. The calcium and the alkali group hypobromites may be prepared by adding bromine to the respective hydroxides in the cold. The free acid is obtained by the action of bromine upon mercuric oxide: $2HgO + 2Br_2 + H_2O = Hg_2OBr_2 + 2HBrO$; also by the action of bromine upon silver nitrate: $AgNO_3 + Br_2 + H_2O = AgBr + HBrO + HNO_3$ (Dancer and Spiller, *C. N.*, 1860, **1**, 38; 1862, **6**, 249). The free acid as an oxidizing agent reacts in many cases similar to free bromine. With **HBr** free **Br** is obtained from both acids (Schoenbein, *J. pr.*, 1863, **88**, 475).

§278. Bromic acid. $HBrO_3 = 128.928$.

$$H'Br^{V}O^{-''}{}_3, \quad H - O - Br \begin{matrix} = O \\ = O \end{matrix}$$

1. **Properties.**—The **anhydride**, Br_2O_5, has not been isolated; and the acid, $HBrO_3$, is known only in solution. It is a colorless liquid, smelling like bromine. It is a strong oxidizing agent. The solution of $HBrO_3$ is decomposed upon boiling, but by evaporating in a vacuum a solution containing about 50 per cent of the acid may be obtained.

2. **Occurrence.**—Neither the acid nor its salts are found in nature.

3. **Formation.**—(*a*) By the electrolysis of **HBr** (Riche, *C. r.*, 1858, **46**, 348). (*b*) By the decomposition of $AgBrO_3$ by **Br**: $5AgBrO_3 + 3Br_2 + 3H_2O = 5AgBr + 6HBrO_3$. (*c*) An alkali bromate is made by adding bromine to a solution of chlorine in sodium carbonate (Kaemmerer, *J. pr.*, 1862, **85**, 452).

4. **Preparation.**—Bromates of **Ba**, **Sr**, **Ca**, **K** and **Na** are made by the action of bromine upon the respective hydroxides at 100°: $6KOH + 3Br_2 = 5KBr + KBrO_3 + 3H_2O$. The free acid is prepared by adding dilute H_2SO_4 in slight excess to $Ba(BrO_3)_2$; the slight excess of H_2SO_4 being removed by the cautious addition of $Ba(OH)_2$.

5. **Solubilities.**—$AgBrO_3$ is soluble in 123 parts of water at 24.5° (Noyes, *Z. phys. Ch.*, 1890, **6**, 246). $Ba(BrO_3)_2$ is soluble in 124 parts of water at ordinary temperature and in 24 parts at 100° (Rammelsberg, *Pogg.*, 1841, **52**, 81 and 86). With the exception of some basic bromates, all other bromates are soluble in water.

6. **Reactions.**—*A.*—**With metals and their compounds.**—Bromic acid is a powerful oxidizing agent, acting in most respects like free bromine. It is usually reduced to hydrobromic acid, sometimes only to free bromine:

1. Hg' becomes Hg'' and a bromide.

2. As''' becomes As^V and a bromide.

3. Sb''' becomes Sb^V and a bromide.

4. Sn'' becomes Sn^{IV} and a bromide.

5. Cu' becomes Cu'' and a bromide.

6. Fe'' becomes Fe''' and a bromide.

7. Mn'' becomes MnO_2 and bromine.

8. Cr''' becomes H_2CrO_4 and bromine.

Silver nitrate precipitates in solutions not very dilute, *silver bromate*, $AgBrO_3$, white, sparingly soluble in water, soluble in ammonium hydroxide, easily soluble by nitric acid, its color and solubility in ammonium hydroxide differing a little from the bromide (§**276**, 5). It is decomposed by hydrochloric acid with evolution of bromine—a distinction from bromides and from other argentic precipitates.

B.—**With non-metals and their compounds.**

1. $H_2C_2O_4$ becomes CO_2 and **Br**. An excess of hot $H_2C_2O_4$ changes the **Br** to **HBr** (Guyard, *Bl.*, 1879, (2), **31**, 299).

HCNS becomes H_2SO_4, **HBr** and other products.

$H_4Fe(CN)_6$ becomes $H_3Fe(CN)_6$ and **HBr**. An excess of $HBrO_3$ carries the oxidation farther.

2. HNO_2 reduces $HBrO_3$, forming HNO_3 and **Br**.

3. PH_3, HH_2PO_2 and H_3PO_3 become H_3PO_4 and **HBr**.

4. **S** and SO_2 become H_2SO_4 and **HBr**.

H_2S forms first **S** then H_2SO_4.

5. **HCl** becomes **Cl** and **Br**.

6. **HBr** forms **Br** from both acids.

7. **HI** becomes **I** and **Br**. With an excess of $HBrO_3$ the products are HIO_3 and **Br** (Kaemmerer, *l. c.*, Wittstein, *Z.*, 1876, **15**, 61).

7. **Ignition.**—All bromates are decomposed upon heating. $KBrO_3$, $NaBrO_3$ and $Ca(BrO_3)_2$ evolve oxygen and leave the bromides. $Co(BrO_3)_2$, $Zn(BrO_3)_2$ and other bromates evolve oxygen and bromine, leaving an oxide.

8. **Detection.**—The bromine is first liberated by some reducing agent that does not carry the reduction to the formation of **HBr**. $H_2C_2O_4$ is a

very suitable agent for this purpose, since it does not change **Br** to **HBr** except when hot and concentrated. The **Br** is detected by CS_2 (§275, 8).

Sulphuric and nitric acids liberate bromic acid from metallic bromates, the $HBrO_3$ remaining for some time intact, and the solution colorless. The gradual decomposition of the $HBrO_3$ is first a resolution into **HBr** and **O**, and as fast as **HBr** is formed it acts with $HBrO_3$, so as to liberate the bromine of both acids. Now, if the solution contained bromide as well as bromate, an abundance of free bromine is obtained *immediately* upon the addition of dilute sulphuric acid in the cold. Hence, if dilute sulphuric acid in the dilute cold solution does not color the carbon disulphide, and if the addition of solution of pure potassium *bromide* immediately develops the yellow color, while it is found that no other oxidizing agent is present, we have corroborative evidence of the presence of a bromate. And, if we treat a solution known to contain bromide with dilute sulphuric acid and carbon disulphide, and obtain no color, we have conclusive evidence of the *absence* of bromates. Hydrochloric acid transposes bromates and quickly decomposes the bromic acid, liberating both bromine and chlorine.

A mixture of *bromate and iodate*, treated with **hydrochloric acid**, furnishes bromine without iodine, coloring carbon disulphide yellow.

The ignited residue of bromates, in all cases if the ignition be done with sodium carbonate, will give the tests for bromides.

9. **Estimation.**—The bromate is reduced to free bromine or to a bromide and determined as such.

§279. Iodine. I = 126.92. Usual valence one, five and seven (§12).

1. **Properties.**—*Specific gravity*, 4.948 at 17° (Gay-Lussac). *Melting point*, 114.2°. *Boiling point*, 184.35° at 760 mm. pressure (Ramsay and Young, *J. C.*, 1886, **49**, 453). At ordinary temperature iodine is a soft gray-black crystalline solid with a metallic lustre. The thin crystals have a brownish-red appearance. Precipitated iodine is a brownish-black powder. It vaporizes very appreciably at ordinary room temperature with a characteristic odor, and may be distilled with steam. The molecule of iodine vapor under about 800° is I_2; above that temperature dissociation takes place, until at 1700° it is complete and the molecule consists of single atoms (Biltz and Meyer, *B.*, 1889, **22**, 725). The vapor of iodine unmixed with other gases is deep blue, mixed with air or other gases it is a beautiful violet. It is sparingly soluble in water to a brown or yellowish-brown solution, which slowly bleaches litmus paper. It stains the skin yellow-brown. The solution gradually decomposes in the sunlight with formation of **HI**. It reacts similarly to bromine and chlorine, but with much less intensity. The free element combines with starch,* forming a compound of an intense blue color. This colored body is quite stable in the cold; decolors upon warming, the color returning upon cooling. The reaction of iodine with starch constitutes a very delicate reaction for the detection of the presence of iodine. It also serves as an indicator in the volumetric estimation of iodine, as all reducing agents destroy the color by taking the iodine into combination. Combined iodine does not react with starch.

*The compound formed when iodine unites with starch is regarded by Bondonneau (*Bl.*, 1877, (2), **28**, 452) as an addition compound of the composition $(C_6H_{10}O_5)_2I$. Mylius (*Ber.*, **20**, 688), gives the formula $[C_{24}H_{40}O_{20}I]_2.HI$ and considers it the hydriodic acid compound of an iodine addition compound of starch. This view is supported by the fact that in the absence of **KI** or other iodide iodine does not give a blue color with starch. (Sonnes, *Z.*, **34**, 409.)

Colorless solutions are formed by all the alkali hydroxides with iodine; the fixed alkali hydroxides forming iodides and iodates. With **ammonia** in water solution it dissolves more slowly, becoming colorless; the solution contains the most of the iodine as ammonium iodide, and deposits a dark-brown powder, termed "*iodide of nitrogen*," very easily and violently *explosive* when dry. According to Chattaway (*Am.*, 1900, **24**, 138) this compound has the composition $N_2H_3I_3$.

The anhydride of iodic acid, I_2O_5, is the only stable compound of iodine and oxygen. The chief acids of iodine are: Hydriodic acid, **HI**; iodic acid, HIO_3; periodic acid, HIO_4.

Hypoiodous acid is said to be formed by the action of alcoholic iodine upon freshly precipitated mercuric oxide (Lippmann, *C. r.*, 1866, **63**, 968). Lunge and Schoche (*B.*, 1882, **15**, 1883) prepared iodide of lime which seemed to contain calcium hypoiodite, $Ca(IO)_2$.

2. **Occurrence.**—Found free in some mineral waters (Wanklyn, *C. N.*, 1886, **54**, 300). As iodides and iodates in sea water (Sonstadt, *C. N.*, 1872, **25**, 196, 231 and 241). In the ashes of sea plants. In small quantities in several minerals, especially in Chili saltpeter as sodium iodate.

3. **Formation.**—From iodides by nearly all oxidizing agents: $2KI + Br_2 = 2KBr + I_2$; and from iodates by nearly all reducing agents: $2HIO_3 + 5H_2C_2O_4 = I_2 + 10CO_2 + 6H_2O$.

4. **Preparation.**—(*a*) The ashes of the sea plants are digested in hot water and from the filtrate most of the salts removed by evaporation and crystallization. The iodides remain in the mother liquor and from this the iodine is obtained by treatment with MnO_2 and H_2SO_4. (*b*) The sodium iodate in the mother liquor of the Chili saltpeter is reduced with SO_2, the iodine precipitated as **CuI** with $CuSO_4$. From the precipitate the iodine is recovered by distillation with MnO_2 and H_2SO_4. By far the greatest portion of the iodine and iodides of commerce is obtained from the Chili saltpeter deposits.

5. **Solubilities.**—It is soluble in about 5500 parts water at 10° to 12° (Wittstein, *J.*, 1857, 123), differing from **Cl** or **Br** in that it forms no hydrate. It is much more soluble in water containing hydriodic acid or soluble iodides. From a concentrated solution in **KI** the compound KI_3 has been obtained. Iodine dissolves in very many organic solvents as alcohol, ether, chloroform, glycerol, benzol, carbon disulphide, etc. Carbon disulphide readily removes the iodine from its solution or suspension in water; with small amounts of iodine imparting to the carbon disulphide a beautiful violet color, with large amounts the CS_2 solution is almost black.

6. **Reactions.**—*A.*—**With metals and their compounds.**—It unites slowly by the aid of heat with **Pb** and **Ag**; more rapidly with **Hg**, **As**, **Sb**, **Sn**, **Bi**, **Cu**, **Cd**, **Al**, **Cr**, **Fe**, **Co**, **Ni**, **Mn**, **Zn**, **Ba**, **Sr**, **Ca**, **Mg**, **K** and **Na**.

In oxidizing metallic compounds the iodine invariably becomes **HI** or an iodide, depending upon whether the mixture be acid or alkaline. It may, however, with certain substances act as a reducing agent, becoming oxidized to iodate or periodate.

1. **Hg′** becomes **Hg″** in acid and in alkaline mixture.

2. **As‴** becomes As^V in presence of alkalis only.

3. **Sb‴** becomes Sb^V in presence of alkalis only.

4. **Sn″** becomes Sn^{IV} in acid or in alkaline mixture.

5. **Cr‴** becomes Cr^{VI} in presence of alkalis only.

6. Fe'' becomes Fe''' in presence of alkalis only.

7. Co'' becomes Co''' in presence of alkalis only.

8. Ni'' is not oxidized.

9. Mn'' becomes Mn^{IV} in presence of alkalis only.

B.—**With non-metals and their compounds.**

1. $K_4Fe(CN)_6$ is oxidized, forming $K_3Fe(CN)_6$ and **KI**, action slow and incomplete.

2. HNO_3 forms HIO_3 and **NO**. Strong HNO_3 must be used (at least *sp. gr.* 1.42). Action is slow. A very good method of making HIO_3.

3. HH_2PO_2 becomes H_3PO_4 with acids and with alkalis.

4. H_2S becomes **S** and **HI**; no action if both substances be perfectly dry (Skraup, *C. C.*, 1896, i, 469) (separation of H_2S from AsH_3). According to Saint-Gilles (*A. Ch.*, 1859, (3), **57**, 221), in alkaline mixture from six to seven per cent of the sulphur is oxidized to a sulphate.

H_2SO_3 becomes H_2SO_4 and **HI**. With a thiosulphate a tetrathionate is formed: $2Na_2S_2O_3 + I_2 = Na_2S_4O_6 + 2NaI$ (Pickering, *J. C.*, 1880, **37**, 128).

5. **Cl** becomes **ICl** or ICl_3, depending upon the amount of chlorine present, water should be absent. In the presence of water **HCl** and HIO_3 are formed; in alkaline mixture a chloride and a periodate: $I_2 + 7Cl_2 + 16NaOH = 14NaCl + 2NaIO_4 + 8H_2O$. $HClO_3$ forms HIO_3 and **HCl**: $5HClO_3 + 3I_2 + 3H_2O = 6HIO_3 + 5HCl$.

6. **Br** becomes **IBr**, decomposed by water (Bornemann, *A.*, 1877, **189**, 183). In alkaline mixture with an excess of **Br** a bromide and an iodate: $I_2 + 5Br_2 + 12KOH = 2KIO_3 + 10KBr + 6H_2O$. $HBrO_3$ becomes **Br** and HIO_3.

7. Iodine combines with **KI** in concentrated solution to form $KI_3(KII_2)$.

7. **Ignition.**—See I.

8. **Detection.**—Iodine is recognized by the yellow to black color when mixed with water; the violet color when dissolved in carbon disulphide; the reddish color when dissolved in chloroform or ether; the blue color when added to a cold solution of starch; the violet color of the vapors, etc. The presence of tannin interferes with the usual tests for iodine unless a drop or two of ferric chloride solution be added (Tessier, *Z.*, 1874, **11**, 313).

9. **Estimation.**—(*a*) It is reduced to an iodide, precipitated with $AgNO_3$, and after drying at 150°, weighed as **AgI**. It is estimated volumetrically with a standard solution of $Na_2S_2O_3$, using starch as an indicator. (*b*) The iodine dissolved in potassium iodide is treated with an alkaline solution of hydrogen peroxide in an azotometer, the oxygen liberated being a measure of the amount of iodine present (Baumann, *Z. angew.*, 1891, 204).

§280. Hydriodic acid. HI = 127.928.

H′I⁻′, H — I.

1. **Properties.**—*Molecular weight*, 127.858. *Vapor density*, 63.927. A colorless incombustible gas. At atmospheric pressure it solidifies at —51°. At 0° it liquefies under a pressure of 3.97 atmospheres (Faraday, *A. Ch.*, 1845, (3), **15**, 266). The constant boiling point of the aqueous solution of the gas is 127°, which solution contains 57 per cent of **HI** and has a *specific gravity* of 1.694 (Roscoe, *J. C.*, 1861, **13**, 160). Gaseous **HI** is dissociated by heat, slowly at 260°; rapidly at 240° (Lemoine, *A. Ch.*, 1877, (5), **12**, 145). Iodine separates from the water solution of the acid when exposed to the air.

2. **Occurrence.**—Not found free in nature, but in combination as iodide or iodate.

3. **Formation.**—(*a*) By direct union of the elements at a full red heat (Merz and Holzmann, *B.*, 1889, **22**, 869). (*b*) By direct union of the elements in presence of platinum black at 300° to 400° (Lemoine, *C. r.*, 1877, **85**, 34). (*c*) From BaI_2 by adding H_2SO_4 in molecular proportions. (*d*) By the action of iodine upon Na_2SO_3 or $Na_2S_2O_3$ (Mène, *C. r.*, 1849, **28**, 478). (*e*) By the action of iodine upon moist calcium hypophosphite: $Ca(H_2PO_2)_2 + 4I_2 + 4H_2O = CaH_4(PO_4)_2 + 8HI$ (Mène, *l. c.*).

Iodides are formed by the direct action of iodine upon the metals; or better, by the action of **HI** upon the oxides, hydroxides or carbonates of those metals whose iodides are soluble in water. Iodides of lead, silver and mercury are formed by precipitation.

4. **Preparation.**—(*a*) By passing H_2S into a mixture of finely divided iodine suspended in water, adding more iodine as fast as the color disappears: $2I_2 + 2H_2S = 4HI + S_2$ (Pellagri, *Gazzetta*, 1875, **5**, 423). (*b*) By bringing moist red phosphorus in contact with iodine: $P_4 + 10I_2 + 16H_2O = 4H_3PO_4 + 20HI$ (Meyer,*B.*, 1887, **20**, 3381). (*c*) By passing vapors of iodine into hot liquid paraffine (Crismer, *B.*, 1884, **17**, 649). (*d*) By heating iodine with copaiba oil (Bruylants, *B.*, 1879, **12**, 2059). It cannot be prepared by adding H_2SO_4 to an iodide and distilling (5).

5. **Solubilities.**—Iodides of lead, silver, mercury and cuprosum are insoluble. Iodides of other ordinary * metals are soluble, those of bismuth, tin and antimony requiring a little free acid to hold them in solution. Lead iodide is sparingly soluble in water (§**57**, 5*c*). Mercuric iodide is readily soluble in excess of potassium iodide, forming a double iodide, K_2HgI_4; most other iodides are more soluble in a solution of potassium iodide than in pure water. The iodides of the alkalis, **Ba**, **Ca** and **Hg**″ are soluble in alcohol; **HgI** and **AgI** are insoluble. All iodides in solution are transposed by **HCl** or by dilute H_2SO_4. Hot concentrated H_2SO_4 decomposes all iodides, those of **Pb**, **Ag** and **Hg** slowly but completely, SO_2 and **I** being produced: $2KI + 2H_2SO_4 = K_2SO_4 + I_2 + SO_2 + 2H_2O$. HNO_3 in excess first transposes then decomposes soluble iodides: $6KI + 8HNO_3 = 6KNO_3 + 3I_2 + 2NO + 4H_2O$. If the HNO_3 be concentrated the iodine is further oxidized: $3I_2 + 10HNO_3 = 6HIO_3 + 10NO + 2H_2O$. Long-continued boiling with HNO_3, *sp. gr.* 1.42, decomposes the insoluble iodides. Chlorine in the cold decomposes all soluble iodides, by heating with chlorine the insoluble iodides are also decomposed: $2KI + Cl_2 =$

* Thallium iodide, **Tl I**, is perfectly insoluble in cold water, a distinction and separation from bromides and chlorides (Huebner, *Z.*, 1872, **11**, 397). Palladous iodide is insoluble in water.

$2KCl + I_2$. With an excess of chlorine the iodine is further oxidized: $I_2 + 5Cl_2 + 6H_2O = 2HIO_3 + 10HCl$. Silver iodide is almost insoluble in ammonium hydroxide or ammonium carbonate (distinction from silver chloride). It is soluble in **KCN**. **AgI** and PbI_2 are soluble by decomposition in solution of alkali thiosulphates: $AgI + Na_2S_2O_3 = NaI + NaAgS_2O_3$. Lead iodide is soluble in a solution of the fixed alkalis.

6. **Reactions.**—*A.*—**With metals and their compounds.**—**Silver nitrate** solution in excess precipitates, from solutions of iodides, *silver iodide*, **AgI**, yellow-white, blackening in the light without appreciable separation of iodine. For solubilities see paragraph above.

Solution of **mercuric chloride** precipitates the bright, yellowish-red to red, *mercuric iodide*, HgI_2. The precipitate redissolves on stirring, after slight additions of the mercuric salt, until equivalent proportions are reached, when its color deepens. For the solubilities of the precipitate see §**58**, 6*f*. Solution of **mercurous nitrate** precipitates *mercurous iodide*, **HgI**, yellow to green (§**58**, 6*f*).

Solution of **lead nitrate** or acetate precipitates, from solutions of iodides not very dilute, *lead iodide*, PbI_2, bright-yellow—soluble, as stated in full in §**57**, 5*c*.

Palladous chloride, $PdCl_2$, precipitates, from solutions of iodides, *palladous iodide*, PdI_2, black, insoluble in water, alcohol or dilute acids, and visible in 500,000 parts of solution. The reagent *does not precipitate bromine* at all in moderately dilute solutions, slightly acidulated with **HCl**. Palladous iodide is slightly soluble in excess of the alkali iodides, and is soluble in ammonium hydroxide (§**106**).

Copper salts precipitate from solutions of iodides *cuprous* iodide (white) mixed with iodine (black): $2CuSO_4 + 4KI = 2CuI + 2K_2SO_4 + I_2$. If sufficient reducing agents (as sulphurous acid) are present to reduce the liberated iodine to **HI**, only the white cuprous iodide will be precipitated (a distinction from bromides and chlorides).

When metals are attacked by **HI** an iodide is formed and hydrogen is evolved. Hydriodic acid unites with all metallic oxides and hydroxides (expect ignited Cr_2O_3) to form iodides; frequently, however, iodine is liberated and an iodide of lower metallic valence is formed:

1. Pb''^{+n} becomes Pb''.

2. As^V becomes As'''; **KI** has no action upon normal K_3AsO_4 (Friedheim and Meyer, *Z. anorg.*, 1891, **1**, 409).

3. Sb^V becomes Sb'''.

4. Bi^V becomes Bi'''.

5. Cu'' becomes Cu'. Soluble iodides reduce normal cupric salts, but have no reducing action in alkaline mixture or upon cupric hydroxide. With phenylhydrazine sulphate and cupric sulphate the iodine of iodides is

completely precipitated (separation from chlorides) (Raikow, *Ch. Z.*, 1894, **18**, 1661).

6. Fe''' becomes Fe'' (§269, 8).

7. Cr^{VI} becomes Cr'''. K_2CrO_4 is not reduced by **KI** even upon boiling the concentrated solutions. $K_2Cr_2O_7$ with **KI** slowly gives **I** and Cr''' in the cold. When **KI** is boiled with a concentrated solution of $K_2Cr_2O_7$ the iodine is completely liberated (separation from bromides and chlorides which are unchanged): $6KI + 5K_2Cr_2O_7 = 8K_2CrO_4 + Cr_2O_3 + 3I_2$ (Dechan, *J. C.*, 1886, **50**, 682; 1887, **51**, 690). When **AgI** is boiled with $K_2Cr_2O_7$ and H_2SO_4 no iodine is evolved, chromium is reduced and the iodide becomes silver iodate: $K_2Cr_2O_7 + AgI + 5H_2SO_4 = 2KHSO_4 + Cr_2(SO_4)_3 + AgIO_3 + 4H_2O$ (Macnair, *J. C.*, 1893, **63**, 1051).

8. Co''^{+n} becomes Co''; **KI** has no reducing action upon cobaltic hydroxide.

9. Ni''^{+n} becomes Ni''; **KI** reduces Ni''', liberating iodine.

10. Mn''^{+n} becomes Mn''. When **KI** is boiled with $KMnO_4$ the manganese becomes MnO_2 and the iodide is oxidized to an iodate: $6KMnO_4 + 3KI + 3H_2O = 3KIO_3 + 6MnO_2 + 6KOH$ (Groeger, *Z. angew.*, 1894, 13 and 52) (distinction from bromides, which do not decolor permanganates).

B.—**With non-metals and their compounds.**

1. $H_3Fe(CN)_6$ forms $H_4Fe(CN)_6$ and **I**; the reaction also takes place in neutral mixture.

2. HNO_2 forms **NO** and **I** (separation of iodide from bromide and chloride) (Jannasch and Aschoff, *Z. anorg.*, 1891, **1**, 144 and 245).

HNO_3 forms **NO** and **I**, with further oxidations to HIO_3 with concentrated HNO_3. The HNO_2 acts much more rapidly than the HNO_3.

3. No reduction with phosphorous compounds.

4. H_2SO_4 dilute no action; with the concentrated acid in excess, SO_2 and **I** are formed: $2KI + 3H_2SO_4 = I_2 + SO_2 + 2KHSO_4 + 2H_2O$; if **KI** be added in excess to *boiling* H_2SO_4, H_2S and **I** are formed: $8KI + 9H_2SO_4 = 4I_2 + H_2S + 8KHSO_4 + 4H_2O$ (Jackson, *J. C.*, 1883, **43**, 339). Ammonium persulphate liberates iodine from iodides at ordinary temperature (Engel, *C. r.*, 1894, **118**, 1263).

5. **Cl** in excess forms **HCl** and HIO_3; with excess of **HI**, **HCl** and **I** are formed. In the presence of a fixed alkali a periodate and a chloride are formed: $KI + 8KOH + 4Cl_2 = 8KCl + KIO_4 + 4H_2O$. Hypochlorous acid oxidizes to iodine, then to iodic in acid solution; in alkaline solution to periodate.

$HClO_3$ with excess of **HI** forms **HCl** and **I**; with excess of $HClO_3$ **HCl** and HIO_3.

6. **Br** forms **I** and **HBr** or a bromide.

$HBrO_3$ with excess of **HI** forms **HBr** and **I**; with excess of $HBrO_3$, **Br** and HIO_3.

7. HIO_3, iodine is liberated from both acids: $HIO_3 + 5HI = 3I_2 + 3H_2O$. HIO_4 gives iodine.

8. H_2O_2 becomes H_2O, **O** and **I** (§**244**, 6*B6*) (Cook, *J. C.*, 1885, **47**, 471).

9. **Ozone** promptly liberates iodine from soluble iodides. Atmospheric oxygen decomposes **HI** and ferrous and calcium iodides slowly, the alkali iodides not at all.

7. **Ignition.**—As a general rule iodides strongly ignited in presence of air and moisture evolve iodine, leaving the oxide of the metal. Ignited in absence of air or moisture the following iodides are not decomposed: **KI**, **NaI**, BaI_2, CaI_2, SrI_2, MnI_2, AlI_3, SnI_4, PbI_2, **AgI** and HgI_2. See Mitscherlich (*Pogg.*, 1833, **29**, 193), Personne (*C. r.*, 1862, **54**, 216) and Gustavson (*A.*, 1873, **172**, 173).

8. **Detection.**—The iodide is oxidized to free iodine by one of the reagents mentioned in (6) above. With a dry powder hot concentrated H_2SO_4 is usually employed when the iodine is detected by the violet fumes evolved, condensing in the cooler portion of the test tube. With solutions the usual reagent is chlorine water. The iodine is recognized by the violet color when shaken with CS_2, or the bright-red color with $CHCl_3$. In case a large amount of iodine be present the CS_2 solution may be almost black. In this case large dilution with CS_2 is necessary to detect the violet color. If but a small amount of iodine be present the chlorine must be added very cautiously or the iodide will all be oxidized to the colorless iodic acid.* With small amounts of iodide, nitric acid is less liable to cause error as relativêly much more nitric acid is required to oxidize the iodine to iodic acid. For the detection of small amounts of iodide a cupric salt strongly acidulated with **HCl** is an excellent reagent for the oxidation: $2CuCl_2 + 2KI = 2CuCl + 2KCl + I_2$. The addition of HNO_2 or $NaNO_2$ to the acid solution will also liberate iodine but not bromine or chlorine. The iodine may then be detected and removed by shaking with CS_2. Bromine and chlorine may then be tested for.

If insoluble iodides are present they should be transposed by H_2S, the insoluble sulphide removed by filtration, the excess of H_2S removed by boiling, and the solution then tested for hydriodic acid. Or the insoluble iodide should be reduced by **Zn** and H_2SO_4: $2AgI + Zn + H_2SO_4 = 2Ag + ZnSO_4 + 2HI$. The filtrate may then be tested for hydriodic acid. The insoluble iodide may also be fused with Na_2CO_3, and after digestion with water the filtrate acidulated and tested for hydriodic acid. That is, the solution must be acidulated before chlorine water is added, else the iodine will be oxidized to an iodate or periodate.

* The test potassium bromide for traces of an iodide it is recommended to add CS_2 and cupric sulphate or a small amount of ferric alum. Or add chlorine water and then a few crystals of ferrous sulphate; then shake with CS_2 (Brito, *C. N.*, 1884, **50**, 210).

9. **Estimation.**—Gravimetrically by precipitation as **AgI** and weighing as such after gentle ignition. Volumetrically by oxidation to iodine and titration with standard $Na_2S_2O_3$ (Gröger, *Z. angew.*, 1894, 52).

§281. Iodic acid. $HIO_3 = 175.928$.

$$H'I^{V}O^{-''}{}_3\,,\ H-O-I\begin{matrix}=O\\=O\end{matrix}$$

1. **Properties.**—Iodic acid is a white crystalline solid; its solution saturated at 14° contains 68.5 per cent HIO_3, and has a *specific gravity* of 2.1629 (Kaemmerer, *Pogg.*, 1869, **138**, 390). At 170° it loses water, forming iodic anhydride, I_2O_5, a white crystalline solid, which, at 300°, dissociates into iodine and oxygen. See Ditte, *A. Ch.*, 1870, (4), **21**, 5. It is readily soluble in water and in alcohol; the solutions redden litmus and afterwards bleach it.

2. **Occurrence.**—The free acid is not found in nature. It is found as $Ca(IO_3)_2$ in sea water, and as sodium iodate in Chili saltpeter (Sonstadt, *C. N.*, 1872, **25**, 196, 231 and 241; Guyard, *Bl.*, 1874, (2), **22**, 60).

3. **Formation.**—(*a*) By electrolyzing a solution of **I** or **HI** (Riche, *C. r.*, 1858, **46**, 348). (*b*) By the action of chlorine on iodine in the presence of much water. The **HCl** formed cannot be expelled by boiling without decomposing the HIO_3. It must be removed by the careful addition of Ag_2O. (*c*) By adding water to ICl_3 and washing with alcohol: $2ICl_3 + 3H_2O = HIO_3 + 5HCl + ICl$. (*d*) KIO_3 is made by treating iodine with **KOH**: $3I_2 + 6KOH = KIO_3 + 5KI + 3H_2O$. And then washing with alcohol to remove the **KI**. (*e*) By heating potassium chlorate and iodine: $10KClO_3 + 6I_2 + 6H_2O = 6KHI_2O_6 + 4KCl + 6HCl$ (Bassett, *J. C.*, 1890, **57**, 760). (*f*) By boiling iodine with barium hydroxide until neutral, filtering and decomposing with sulphuric acid (Stevenson, *C. N.*, 1877, **36**, 201). (*g*) By the action of **I** upon $AgNO_3$: $5AgNO_3 + 3I_2 + 3H_2O = 5AgI + 5HNO_3 + HIO_3$.

Iodates of the alkalis and alkaline earths are easily made by the action of iodine on the hydroxides, and separation by alcohol or by crystallization from the iodides which are formed in the reaction. All iodates may be made by action of the acid on the hydroxides or carbonates.

4. **Preparation.**—(*a*) Iodine is oxidized by boiling with nitric acid *sp. gr.* 1.52, and removing the excess of the nitric acid by evaporation. (*b*) By adding a slight excess of H_2SO_4 to $Ba(IO_3)_2$ and removal of the excess of H_2SO_4 by the careful addition of $Ba(IO_3)_2$. (*c*) By boiling a solution of potassium iodide with an excess of potassium permanganate in neutral or alkaline solution: $KI + 2KMnO_4 + H_2O = KIO_3 + 2KOH + 2MnO_2$ (Gröger, *Z. angew.*, 1894, 13 and 52). (*d*) The very stable potassium biiodate, KHI_2O_6, is formed by recrystallizing a water solution of equal portions of KIO_3 and HIO_3. It is soluble in 18.66 parts water at 17° (Meineke, *A.*, 1891, **261**, 359).

5. **Solubilities.**—$Ba(IO_3)_2$ is soluble in about 3000 parts water at ordinary temperature; and in about 600 parts at 100° (Kremers, *Pogg.*, 1851, **84**, 27; Spica, *Gazzetta*, 1894, **24**, i, 91). $AgIO_3$ is soluble in 27,700 parts of water at 25°; in 2.1 parts NH_4OH (10 per cent) at 25° (separation from silver iodide); in 1044.3 parts HNO_3, *sp. gr.* 1.21 at 25° (Longi, *Gazzetta*, 1883, **13**, 87). The iodates of **Ag**, **Ba**, **Pb**, **Hg**, **Sn**, **Bi**, **Cd**, **Fe** and **Cr** require at 15° more than 500 parts of water for their solution and the following require less: **Cu**, **Al**, **Co**, **Ni**, **Mn**, **Zn**, **Sr**, **Ca**, **Mg**, **K** and **Na**. They are all transposed by concentrated HNO_3 or H_2SO_4; and are decomposed by concentrated **HCl**. They are soluble in the alkalis in so far as

the corresponding metallic oxides are soluble in those reagents. Most of the iodates are insoluble in alcohol (with **K**, **Na**, **Ba** and **Ca** iodates a separation from iodides).

6. **Reactions.**—*A.*—**With the metals and their compounds.**—A few metals are attacked evolving hydrogen, forming iodates, sometimes traces of iodides. With the following metallic compounds the valence of the metal is changed:

1. **As‴** becomes **As^{V}** with liberation of iodine. **AsH_3** in excess forms **As°**, with the **HIO_3** in excess **As^{V}** (Ditte, *A.*, 1870, **156**, 336).

2. **Sb‴** becomes **Sb^{V}** with liberation of iodine. **SbH_3** forms **Sb°**.

3. **Sn″** becomes **Sn^{IV}** and **HI**.

4. **Cu′** becomes **Cu″** with liberation of iodine.

5. **Fe″** becomes **Fe‴** with liberation of iodine.

Solution of **silver nitrate** precipitates, from even very dilute solutions of iodates and from solutions of iodic acid if not very dilute, *silver iodate*, **$AgIO_3$**, white, crystalline, soluble in ammonium hydroxide, soluble in an excess of hot **HNO_3**. *In the ammoniacal solution*, **hydrosulphuric acid** forms silver sulphide, sulphur and ammonium iodide.

Barium chloride precipitates *barium iodate*, **$Ba(IO_3)_2$**, slightly soluble in cold, more soluble in hot water, insoluble in alcohol, soluble in hot dilute nitric acid, readily soluble in cold dilute hydrochloric acid. Hence, dilute solutions of free iodic acid should either be neutralized or tested with barium nitrate. This precipitate, by addition of alcohol, is a complete *separation from iodides*, and, when well washed, decomposed with a very little sulphurous acid (8), and found to color carbon disulphide violet, its evidence for iodic acid is conclusive. Barium iodate is transposed by ammonium carbonate.

Salts of **lead** give a white precipitate of *lead iodate*, **$Pb(IO_3)_2$**. Ferric chloride gives, in solutions not dilute, a yellowish-white precipitate of *ferric iodate*, **$Fe(IO_3)_3$**, sparingly soluble in water, and freely *soluble in excess of the reagent*. Boiling decomposes it.

Alcohol precipitates *potassium iodate* from water solution, an approximate separation from iodide.

B.—**With non-metals and their compounds.**

1. **$H_2C_2O_4$** becomes **CO_2** and **I**. Action is slow unless solutions are hot. Carbon (except diamond) heated in sealed tubes becomes **CO_2** with separation of **I** (Ditte, *l. c.*).

$H_4Fe(CN)_6$ becomes **$H_3Fe(CN)_6$** and **I**.

HCNS forms **H_2SO_4**, **I** and some other products.

2. **HNO_2** becomes **HNO_3** and **I**.

3. **PH_3** becomes **H_3PO_4** and **I**. With an excess of **PH_3**, **HI** is formed.

Water in which phosphorus has stood reduces iodic acid to iodine (Corne, *J. Pharm.*, 1878, (4), **28**, 386).

HH_2PO_2 becomes H_3PO_4 and **I**.

4. H_2S becomes **S** and **I**. Thiosulphates form first iodine, then an iodide. H_2SO_3, with excess of HIO_3, becomes H_2SO_4 and **I**; with excess of H_2SO_3, H_2SO_4 and **HI**.

5. **HCl**, if concentrated, forms ICl_3 and **Cl**, iodine not being liberated.

6. **HBr** forms **Br** and **I**.

7. **HI** forms **I** from both acids. The addition of tartaric acid to a mixture of **KI** and KIO_3 is sufficient to give an *immediate* test for free iodine with CS_2. It must be remembered that an iodide alone rendered acid will give a test for free iodine after a short time.

8. Morphine reduces iodic acid with separation of iodine.

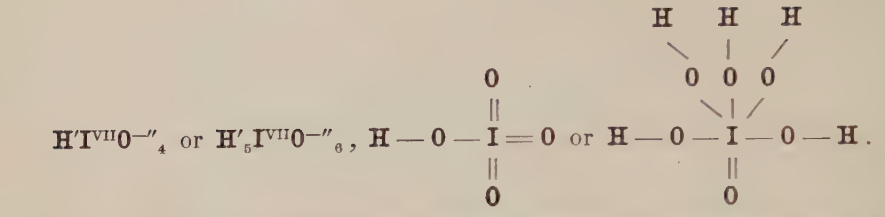
7. **Ignition.**—Potassium and sodium iodates on ignition form iodides and evolve oxygen (Cook, *J. C.*, 1894, **65**, 802). Many other iodates evolve oxygen but the iodide formed is further decomposed as stated in §**275**, 7.

Iodates *in dry mixture* with combustible bodies are reduced, on heating or concussion, with *detonation*, but much less violently than chlorates or nitrates.

8. **Detection.**—It is usually detected, after acidulation, by treatment with some reducing agent for the formation of free iodine. H_2SO_3 is often employed because it acts rapidly and in the cold; but traces of HIO_3 frequently escape detection for the least excess of H_2SO_3 at once reduces the iodine to colorless hydriodic acid. A desirable reagent for this reduction is one that will act rapidly in the cold, and in no case cause the further reduction to hydriodic acid. The following reducing agents have been used: $K_4Fe(CN)_6$ acidulated with dilute H_2SO_4, H_3AsO_3, **CuCl**, $FeSO_4$, morphine sulphate and uric acid. To detect KIO_3 in **KI** it is recommended by Schering (*J. C.*, 1873, **26**, 191) to add a crystal of tartaric acid to the solution. The formation of a yellow zone is indicative of an iodate. Hydrochloric acid may be used, but if it contains a trace of chlorine it will give the test for an iodate. Iodine frequently occurs in nitric acid as iodic acid. Hilzer (*J. C.*, 1876, **29**, 442) directs to add equal volumes of water, carbon disulphide, and then coarse zinc filings. It may be necessary to warm the solution slightly. Biltz (*C. C.*, 1877, 86) dilutes the HNO_3 with water, adds starch solution and then H_2S solution drop by drop. A blue zone is formed if HIO_3 be present.

9. **Estimation.**—(*a*) By precipitation with $AgNO_3$, and after drying at 100° weighing as $AgIO_3$. (*b*) By reducing to an iodide and estimating as such. (*c*) By treating with **KI** acidulated with H_2SO_4, and titrating the iodine liberated with standard $Na_2S_2O_3$.

§282. Periodic acid. $HIO_4 = 191.928$.



The anhydride, I_2O_7, has not been isolated, and but one acid is known in the free condition, $HIO_4,2H_2O$ or H_5IO_6. This acid exists in colorless monoclinic crystals, which do not lose water at 100°. It melts at 133°, and at a higher temperature it decomposes into iodic anhydride, water and oxygen (Kimmins, *J. C.*, 1887, **51**, 356; and 1889, **55**, 148). Numerous periodates have been prepared as if derived from one or the other following named acids: HIO_4, H_3IO_5, H_5IO_6, $H_4I_2O_9$, $H_8I_2O_{11}$, $H_{12}I_2O_{13}$, $H_{10}I_4O_{19}$, $H_{10}I_6O_{26}$ (Rammelsberg, *Pogg.*, 1865, **134**, 368, 499).

The free periodic acid, H_5IO_6, is prepared: (*a*) By oxidizing iodine with perchloric acid: $2HClO_4 + I_2 + 4H_2O = 2H_5IO_6 + Cl_2$ (Kaemmerer, *Pogg.*, 1869, **138**, 406). (*b*) By heating iodine or barium iodide with a mixture of barium oxide and barium peroxide, digesting with water, and transposing the $Ba_5(IO_6)_2$ thus obtained with the calculated amount of sulphuric acid (Rammelsberg, *Pogg.*, 1869, 137, 305). (*c*) By conducting chlorine into sodium iodate in presence of sodium hydroxide: $NaIO_3 + 3NaOH + Cl_2 = Na_2H_3IO_6 + 2NaCl$. This acid periodate dissolved in water with a little nitric acid and then precipitated with silver nitrate, forms the silver salt, $Ag_2H_3IO_6$. This precipitate is dissolved in nitric acid and evaporated on the water-bath, when orange-colored crystals of silver meta periodate are formed according to the following: $2Ag_2H_3IO_6 + 2HNO_3 = 2AgIO_4 + 2AgNO_3 + 4H_2O$. Water decomposes this precipitate: $2AgIO_4 + 4H_2O = H_5IO_6 + Ag_2H_3IO_6$. Or the silver periodate, $AgIO_4$, is decomposed by Cl or Br (Kaemmerer, *l. c.*, p. 390).

The silver salts vary in color: $AgIO_4$ is orange; Ag_2HIO_5, dark brown; $Ag_4I_2O_9$, chocolate colored; while silver iodate is white (a distinction). In the general reactions periodic acid and periodates resemble iodic acid and iodates.

$H_2C_2O_4$ becomes CO_2 and I.

H_3PO_2 becomes H_3PO_4 and HI.

H_2S becomes S and HI.

H_2SO_3 becomes H_2SO_4 and HIO_3 without separation of iodine when the two acids are present in molecular proportions. The presence of a greater proportion of H_2SO_3 causes, first, separation of iodine with final complete reduction to HI (Selmous, *B.*, 1888, **21**, 230):

$$HIO_4 + H_2SO_3 = HIO_3 + H_2SO_4$$
$$3HIO_4 + 8H_2SO_3 = HIO_3 + I_2 + 8H_2SO_4 + H_2O$$
$$2HIO_4 + 7H_2SO_3 = I_2 + 7H_2SO_4 + H_2O$$
$$HIO_4 + 4H_2SO_3 = HI + 4H_2SO_4$$

HCl becomes Cl and ICl_3

HI forms I from both acids.

According to Lautsch (*J. pr.*, 1867, **100**, 86), its behavior with mercurous nitrate is characteristic. The pentasodic periodate, Na_5IO_6, gives a light-yellow precipitate, Hg_5IO_6.

§283. Comparison of Certain Reactions of the Acids of Chlorine, Bromine and Iodine (§13).

Taken in Aqueous Solution, as Potassium Salts, or other Soluble Compounds.

	Chlorides.	Bromides.	Iodides.	Chlorates.	Bromates.	Iodates.	Hypochlorites
$AgNO_3$, in excess.	**AgCl**, white.	**AgBr**, white.	**AgI**, yellow-white.	No precipitate.	No precipitate.	**$AgIO_3$**, white.	No precipitate.
$AgNO_3$, excess of the solution tested.	Precipitate.	Precipitate.	Sparingly soluble.	.....	... .	Precipitate.	.....
NH_4OH, to the silver precipitate.	Dissolved.	Dissolved.	Not dissolved.	.....	.....	Dissolved.	.....
$HgCl_2$, in excess.	.....	No precipitate.	**HgI_2**, yellow-red.	No precipitate.	No precipitate.	**$Hg(IO_3)_2$**.	No precipitate.
$HgCl_2$, excess of the solution tested.	.....	No precipitate.	No precipitate.	.....	.....	Precipitate.	
$HgNO_3$, excess.	**HgCl**, white.	**HgBr**, white.	**HgI**, green.	No precipitate.	Unstable.	Precipitate.	No precipitate.
$BaCl_2$.	.....	.....	.....	.....	.....	**$Ba(IO_3)_2$**.	
$CuSO_4$, with **H_2SO_3**.	.....	.....	**CuI**.	.....	.....	**CuI**.	
H_2SO_4, dilute.	**HCl**, gas, soluble	**HBr**, gas, soluble.	**HI**, gas soluble.	**$HClO_3$**.	**$HBrO_3$**, unstable.	**HIO_3**.	**Cl**, bleaches, § **271**, 8.
HCl.	.....	**HBr**.	**HI**.	**Cl**, §**273**, 6*B5*.	**Br** and **Cl**.	**HIO_3**.	**Cl**.
Cl.	.....	**Br**.	**I** then **HIO_3**.				
Br.	.....	.....	**I**.				
HI.	.....	.....	.....	**HIO_3** and **HCl**.	**Br** and **I**, or **HIO_3**.	**I** § **281**, 6*B7*.	
Chromate, with **H_2SO_4**.	**CrO_2Cl_2**. §**269**, 8*d*.	**Br**. § **276** 6*A6*.	**I**.				
$KMnO_4$, dilute neutral.	.....	.....	**I**, then **KIO_3**.				
Na_2SO_3, with **H_2SO_4**.	.....	.....	.....	**HCl**.	**HBr**.	**HI**.	**HCl**.
H_2S.	.....	.....	.....	**HCl** and **S**, then **H_2SO_4**.	**HBr** and then **H_2SO_4**.	**Hl** and **S**.	**HCl** and **S**, then **H_2SO_4**.

PART IV.—SYSTEMATIC EXAMINATIONS.

REMOVAL OF ORGANIC SUBSTANCES.

§284. Before the liquid reagents can be applied, solids must be dissolved. The methods of inorganic analysis do not provide against interference by organic compounds; and, in general, it is impossible to conduct inorganic analysis in material containing organic bodies. It is, therefore, first necessary to ascertain if the unknown substance contains organic matter. This has been ascertained in the preliminary examination by the blackening or charging of the substance when heated in the closed tube. A burnt odor is also excellent evidence of the presence of organic matter. If organic matter is found to be present, it may be removed as follows: 1st, by combustion at a red or white heat, with or without oxidizing reagents; 2d (in part), by oxidation with potassium chlorate and hydrochloric acid on the water-bath (§69, 6′*c1*); 3d, by oxidation with nitric acid in presence of sulphuric acid, at a final temperature of the boiling point of the latter (§79, 6′*c3*); 4th, by solvents of certain classes of organic substances; 5th, by dialysis. These operations are conducted as follows:

§285. *Combustion at a red or white heat*, of course, excludes analysis for mercury, arsenous and antimonous bodies (except as provided in §70, 7), and ammonium. The last-named constituent can be identified from a portion of the material in presence of the organic matter (§207, 3). If chlorides are present some iron will be lost at temperatures above 100°, and potassium and sodium waste notably at a white heat, and slightly at a full red heat. Certain acids will be expelled, and oxidizing agents reduced.

The material is thoroughly dried and then heated in a porcelain or platinum crucible, at first gently. It will blacken, by separation of the carbon of the organic compounds. The ignition is continued until the black color of the carbon has disappeared. In special cases of analysis, it is only necessary to char the material; then pulverize it, digest with the suitable solvents, and filter; but this method does not give assurance of full separation of all substances. Complete combustion, without use of oxidizing agents, is the way most secure against loss, and entailing least change of the material: it is, however, sometimes very slow. The operation may be hastened, with oxidation of all materials, by *addition of nitric acid, or of ammonium nitrate*. The material is first fully charred; then allowed to cool till the finger can be held on the crucible; enough nitric acid to moisten the mass is dropped from a glass rod upon it, and the heat of the water-bath continued until the mass is dry, when it may be very gradually raised to full heat. This addition may be repeated as necessary. The ammonium nitrate may be added, as a solid, in the same way. The residue is treated according to §301.

§286. *Oxidation with potassium chlorate and hydrochloric acid on the water-bath* does not wholly remove organic matter, but so far disintegrates and changes it that the filtrate will give the group precipitates, pure enough for most tests. It does not vaporize any bases but ammonium, but of course oxidizes or chlorinates all constituents. It is especially applicable to viscid liquids; it may be followed by evaporation to dryness and ignition, according to the paragraph above.

The material with about an equal portion of hydrochloric acid is warmed on the water-bath, and a minute portion of potassium chlorate is added at short intervals, stirring with a glass rod. This is continued until the mixture is wholly decolored and dissolved. It is then evaporated to remove chlorine, diluted and filtered. If potassium and chlorine are to be tested for, another portion may be treated with nitric acid, on the water-bath. The organic matter left from the action of the chlorine or the nitric acid may be sufficient to prevent the precipitation of aluminum and chromium in the third group of bases; so that a portion must be ignited. As to arsenic and antimony, see §70, 7.

§287. The action of *sulphuric with nitric acid at a gradually increasing heat* leaves behind all the metals (not ammonium), with some loss of mercury and arsenic (and iron?) if chlorides are present in considerable quantity. In this, as in the operations before mentioned, volatile acids are lost; sulphides partly oxidized to sulphates, etc.

The substance is placed in a tubulated retort, with about four parts of concentrated sulphuric acid, and gently heated until dissolved or mixed. A funnel

is now placed in the tubulure, and nitric acid added in small portions, gradually raising the heat, for about half an hour—so as to expel the chlorine, and not vaporize chlorides. The material is now transferred to a platinum dish and heated until the *sulphuric acid begins to vaporize*. Then add small portions of nitric acid, at intervals, until the liquid ceases to darken by digestion, after a portion of nitric acid is expelled. Finally, evaporate off nearly all of the sulphuric acid, using the lowest possible heat at the close. Cool and dilute with a few c.c. of water. If a residue remains undissolved boil for a few minutes, cool, filter and wash with dilute sulphuric acid. The residue will contain (*a*) undecomposed mineral matter such as silicates, (*b*) all the lead, strontium and barium as sulphates, (*c*) some of the calcium, bismuth, antimony and tin and (*d*) practically all of the chromium as the insoluble anhydrous sulphate.

§288. *The solvents used* are chiefly *ether for fatty matter*, and alcohol or ether, or both successively, for resins. Instead of either of these, benzol may be used; and many fats and some resins may be dissolved in petroleum ether. It will be observed that ether dissolves some metallic chlorides, and that alcohol dissolves various metallic salts. Before the use of either of these solvents upon solid material, it should be thoroughly dried and pulverized. Fatty matter suspended in water solutions may be approximately removed by filtering through wet, close filters; also by shaking with ether or benzol, and decanting the solvent after its separation.

§289. *By Dialysis*, the larger part of any ordinary inorganic substance can be extracted in approximate purity from the greater number of organic substances in water solution. The degree of purity of the separated substance depends upon the kind of organic material. Thus albuminoid compounds are almost fully rejected; but saccharine compounds pass through the membrane quite as freely as some metallic salts. (Consult *Watts' Dictionary*, 1894, **IV**, 172).

PRELIMINARY EXAMINATION OF SOLIDS.*

§290. Before proceeding to the analysis of a substance in the wet way, a careful study should usually be made of the reactions which the substance undergoes in the solid state, when subjected to a high heat, either alone or in the presence of certain reagents, before the blow-pipe, or in the flame of the Bunsen burner. This examination in the dry way precedes that in the wet, and should be carried on systematically, following the plan laid down in the tables, and noting carefully every change which the substance under investigation undergoes, and if necessary making reference to some of the standard works on blow-pipe analysis. In order to understand fully the nature of these reactions, the student should first acquaint himself with the character of the different parts of the flame, and the use of the blow-pipe in producing the reducing and oxidizing flames.

§291. *The flame of the candle, or of the gas-jet*, burning under ordinary circumstances, consists of three distinct parts: a dark nucleus or zone in the centre, surrounding the wick, consisting of unburnt gas—a luminous cone surrounding this nucleus, consisting of the gases in a state of incomplete combustion. Exterior to this is a thin, non-luminous envelope, where, with a full supply of oxygen, complete combustion is taking place: here we find the hottest part of the flame. The non-luminous or outer part is called the **oxidizing flame**; the luminous part, consisting of carbon and unconsumed hydrocarbons, is called the **reducing flame.**

§292. *The flame produced by the blow-pipe* (or Bunsen burner) is divided into two parts: the oxidizing flame, where there is an excess of oxygen, corresponding to the outer zone of the candle-flame; and the reducing flame, where there is an excess of carbon, corresponding to the inner zone of the candle-flame. Upon the student's skill in producing these flames depend very largely the results in the use of the blow-pipe.

In order to produce a good **oxidizing flame**, the jet of the blow-pipe is placed just within the flame, and a moderate blast applied the air being thoroughly mixed with the gas, the inner blue flame, corresponding to the exterior part

* If the unknown is a solution the solid may be obtained by evaporation on the water bath.

of the candle-flame, is produced: the hottest and most effective part is just before the apex of the blue cone, where combustion is most complete.

The **reducing flame** is produced by placing the blow-pipe just at the edge of the flame, a little above the slit, and directing the blast of air a little higher than for the oxidizing flame. The flame assumes the shape of a luminous cone, surrounded by a pale-blue mantle; the most active part of the flame is somewhat beyond the apex of the luminous cone.

§293. The blast with the blow-pipe is not produced by the lungs, but by the action of the muscles of the cheek alone. In order to obtain a better knowledge of the management of the flame, and to practise in producing a good reducing flame, it is well to fuse a small grain of metallic tin upon charcoal, and raising to a high heat endeavor to prevent its oxidation, and keep its surface bright: or better, perhaps, to dissolve a speck of manganese dioxide in the borax bead on platinum wire—the bead becoming amethyst-red in the outer flame and colorless in the reducing flame. The beginner should work only with substances of a known composition, and not attempt the analysis of unknown complex substances, until he has made himself perfectly familiar with the reactions of at least the more frequently occurring elements.

The amount of substance taken for analysis should not be too large: a quantity of about the bulk of a mustard-seed being, in most cases, quite sufficient.

The physical properties of the substance under examination are to be first noted; such as color, structure, odor, lustre, density, etc.

Heat in Glass Tube Closed at One End.

§294. The substance, in fragments or in the form of a powder, is introduced into a small glass tube, sealed at one end, or into a small matrass, and heat applied gently, gradually raising it to redness, if necessary with the aid of the blow-pipe. When the substance is in the form of a powder it is more easily introduced into the tube by placing the powder in a narrow strip of paper, folded lengthwise in the shape of a trough: the paper is now inserted into the tube held horizontally, the whole brought to a vertical position, and the paper withdrawn; in this way the powder is all deposited at the bottom of the tube. By this treatment in the glass tube we are first to notice whether the substance undergoes a change, and whether this change occurs with or without decomposition. The sublimates, which may be formed in the upper part of the tube, are especially to be noted. Escaping gases or vapors should be tested as to their alkalinity or acidity, by small strips of moist red and blue litmus paper inserted in the neck of the tube.

Heat in Glass Tube Open at Both Ends.

§295. The substance is inserted into a glass tube from two to three inches long, about one inch from the end, at which point a bend is sometimes made; heat is applied gently at first, the force of the air-current passing through the tube being regulated by inclining the tube at different angles. Many substances undergoing no change in the closed tube absorb oxygen and yield volatile acids or metallic oxides. As in the previous case, the nature of the sublimate and the odor of the escaping gas are particularly to be noted. The reactions of sulphur, arsenic, antimony and selenium are very characteristic; these metals, if present, are generally easily detected in this way (§69, 7).

Heat in Blow-pipe Flame on Charcoal.

§296. For this test, a well-burned piece of charcoal is selected, and a small cavity made in the side of the coal; a small fragment of the substance is placed in the cavity, and, if the substance be a powder, it may be moistened with a drop of water. The coal is inclined at an angle of about twenty-five degrees and the flame made to play horizontally upon the assay. The substance is first heated in the oxidizing flame and then in the reducing flame. Any metallic beads which form are allowed to cool and carefully examined for malleability, fusibility and color.

Any escaping gases are to be tested for their odor; the changes of color which the substance undergoes, and the nature and color of the coating which may form near the assay, are also to be carefully noted. Some substances, as lead, may be detected at once by the nature of the coating.

Ignition of the Substance previously Moistened with a Drop of Cobalt Nitrate.

§297. This test may be effected either by heating on charcoal, in the loop of platinum wire, or in the platinum-pointed forceps. A portion of the substance is moistened with a drop of the reagent, and exposed to the action of the outer flame. When the substance is in fragments, and porous enough to absorb the cobalt solution, it may be held in the platinum-pointed forceps and ignited. The color is to be noted after fusion. This test is rather limited; aluminum, zinc and magnesium giving the most characteristic reactions.

Fusion with Sodium Carbonate on Charcoal.

§298. The powdered substance to be tested is mixed with sodium carbonate, moistened and placed in the cavity of the coal. Some substances form, with sodium carbonate at a high heat, fusible compounds; others infusible. Many bodies, as silicates, require fusion with alkali carbonate before they can be tested in the wet way. Many metallic oxides are reduced to metal, forming globules, which may be easily detected.

When this test is applied for the detection of sulphates and sulphides, the flame of the alcohol lamp is to be substituted for that of the gas-flame, as the latter generally contains sulphur compounds.

Examination of the Color which may be imparted to the Outer Flame.

§299. In this way many substances may be definitely detected. The test may be applied either on charcoal or on the loop of platinum wire, preferably in the latter way. When the substance will admit a small fragment is placed in the loop of the platinum wire, or held in the platinum-pointed forceps, and the point of the blue flame directed upon it. If the substance is in a powder it may be made into a paste with a drop of water, and placed in the cavity of the charcoal, the flame being directed horizontally across the coal. The color which the substance imparts to the outer flame in either case is noted. In most cases the flame of the Bunsen burner alone will suffice; the substance being heated in the loop of platinum wire, which, in all cases, should be first dipped in hydrochloric acid and ignited, in order to secure against the presence of foreign substances. Those salts which are more volatile at the temperature of the flame, as a rule give the most intense coloration. When two or more substances are found together it is sometimes the case that one of them masks the color of all the others; the bright yellow flame of sodium, when present in excess, generally veiling the flame of the other elements. In order to obviate this, colored media, as cobalt-blue glass, indigo solution, etc., are interposed between the flame and the eye of the observer. The appearance of the flame of various bodies, when viewed through these media, enables us often to detect very small quantities of them in the presence of large quantities of other substances.

Treatment of the Substance with Borax and Microcosmic Salt.

§300. This is best effected in the loop of platinum wire. This is heated and dipped into the borax or microcosmic salt and heated to a colorless bead; a small quantity of the substance under examination is now brought in contact with the hot bead, and heated, in both the oxidizing and reducing flames. Any reaction which takes place during the heating must be noticed; most of the metallic oxides are dissolved in the bead, and form a colored glass, the color of which is to be observed, both while hot and cold. The color of the bead varies in intensity, according to the amount of the substance used; a very

small quantity will, in most cases, suffice. Certain bodies, as the alkaline earths, dissolve in borax, forming beads which, up to a certain degree of saturation, are clear. When these beads are brought into the reducing flame, and an intermittent blast used, they become opaque. This operation is called **flaming.**

As reducing agents, certain metals are employed in the bead of borax or microcosmic salt. For this purpose **tin** is generally chosen, *lead* and *silver* being taken in some cases. These metals cannot be used in the loop of platinum wire, as they will alloy the platinum. The beads are first formed in the loop of wire; then, while hot, shaken off into a porcelain dish, several being so obtained. A number of these are now taken on charcoal and fused into a large bead, which is charged with the substance to be tested, and then with the tin or other metal. For this purpose tin foil (or lead foil) is previously cut in strips half an inch wide, and the strips rolled into rods. The end of the rod is touched to the hot bead to obtain as much of the metal as required. Lead may be added as precipitated lead ("proof-lead"), and silver as precipitated silver. By aid of tin in the bead, cuprous oxide, ferrous oxide and metallic antimony are obtained and other reductions effected, as directed in §77, 7, and elsewhere.

CONVERSION OF SOLIDS INTO LIQUIDS.

§301. Before the fluid reagents can be applied, solids must be dissolved. To obtain a complete solution, the following steps must be observed:

First. The solid remaining after removal of organic matter, or in the absence of organic, the entire solid, is treated as follows unless it is a metal or alloy (see §303). The solid, reduced to a fine powder, is boiled in ten times its quantity of **water.** Should a residue remain, it is allowed to subside, and the clear liquid poured off or separated by filtration. A *drop* or *two* evaporated on glass, or clean and bright platinum foil, will give a residue, if any portion has dissolved. If a solution is obtained, the residue, if any, is exhausted, and well washed with hot water.

Second. The residue, insoluble in water, is digested some time with hot **hydrochloric acid.** (Observe §305.) The solid, if any remain, is separated by filtration and washed, first with a little of this acid, then with water. The solution, with the washings, is reserved.

Third. The well-washed residue is next digested with hot **nitric acid.** Observe if there are vapors of nitrogen oxides, indicating that a metal or other body is being oxidized. Observe if sulphur separates. If any residue remains it is separated by filtration and washing, first with a little acid, then with water, and the solution reserved.

Sometimes it does not matter which acid is used first. But if a first-group base be present, HNO_3 should be added first, for **HCl** would form an insoluble chloride. If the substance contain tin (especially an alloy of tin) HNO_3 would form insoluble metastannic acid, $H_{10}Sn_5O_{15}$, in which case **HCl** should be used first.

Fourth. Should a residue remain it is to be digested with **nitrohydrochloric acid,** as directed for the other solvents.

The acid solutions are to be evaporated nearly to dryness, and then redissolved in water, acidulating, if necessary, to keep the substance in solution.

Fifth. Should the substance under examination prove insoluble in acids, it is likely to be either a sulphate (of barium, strontium or lead); a chloride, or bromide, of silver or lead; a silicate or fluoride—perhaps decomposed by sulphuric acid—and it *must be fused with a fixed alkali carbonate,* when the constituents are transposed in such manner as to render them soluble. The water solution of the fused mass will be found to contain the acid; the residue, insoluble in water, the metal, now soluble in hydrochloric or nitric acids (compare §266, 7).

If more than one solution is obtained, by the several trials with solvents, the material contains more than one compound, and the solutions, as separated by filtration, should be preserved separately, as above directed, and analyzed separately. *The separate results, in many cases, indicate the original combination of each metal.*

TREATMENT OF A METAL OR AN ALLOY.

§303. As most metals are converted into soluble compounds by nitric acid, this is the best acid to use for the solution of metals and alloys. Of the common metals, all are oxidized and all, except tin, arsenic and antimony are converted into nitrates which are soluble in water. Arsenic is converted by strong nitric acid into arsenic acid which is readily soluble in water. Antimony is converted into the pentoxide which is insoluble in water or nitric acid and tin is converted into metastannic acid which is also insoluble in water and nitric acid. When an alloy containing antimony and, especially, tin is treated with nitric acid, considerable portions of the other metals remain in the insoluble residue with the tin and antimony. The action of nitric acid on these metals may be represented as follows:

$$6Sb + 10HNO_3 = 3Sb_2O_5 + 10NO + 5H_2O\,.$$
$$15Sn + 20HNO_3 + 5H_2O = 3H_{10}Sn_5O_{15} + 20NO\,.$$
$$3Pb + 8HNO_3 = 3Pb(NO_3)_2 + 2NO + 4H_2O\,.$$
$$Bi + 4HNO_3 = Bi(NO_3)_3 + NO + 2H_2O\,.$$

Gold and platinum are not attacked by nitric acid. Of the rare elements, titanium and tungsten are converted into insoluble hydroxides like tin, tungsten being converted into the yellow insoluble tungstic acid (H_2WO_4). Alloys may also contain such insoluble constituents as ferro-chrome or ferrosilicon which separate as a black residue.

Carbon, as well as gold and platinum, also remains as a black insoluble residue.

Method of Procedure.

About one gram of the metal or alloy in the form of sawings or drillings is placed in a beaker. Add 10 cc. concentrated nitric acid and 5 cc. water. Cover the beaker with a watch crystal and warm on the water bath until action ceases. If any of the alloy remains unacted upon add a little more nitric acid and water and continue the heating. When the action is complete evaporate to dryness on the waterbath. Add 5 cc. concentrated HNO_3 and 20 cc. water, digest on the water bath, filter, and wash the residue. The solution is tested for the metals of all the groups.

The residue is digested in strong hydrochloric acid and if necessary in aqua regia. If a residue still remains it may be silicic, titanic or tungstic acid. Transfer to a platinum crucible and add a few cc. of hydrofluoric acid and warm under a hood. Silicic acid is volatilized. Add a few drops of H_2SO_4 and warm until the hydrofluoric acid is volatilized. Titanium and tungsten dissolve on diluting with water. If a considerable residue still remains, it is probably metastannic acid. Filter this and wash and transfer the paper with the precipitate to a porcelain crucible, supported on a pipestem triangle, and burn the paper.

Add six times the weight of the precipitate of a mixture of equal parts of sulphur and dry sodium carbonate. Place the lid on the crucible and heat with a small flame of the Bunsen burner until the sulphur melts. Continue the heating until the blue flame of the burning sulphur which escapes around the lid of the crucible is almost gone. Allow the crucible to cool with the lid on. Place the crucible with its contents in a beaker and dissolve the fused mass in warm water. The tin will be in the solution as sodium thiostannate. Any insoluble sulphides of copper, lead, etc., are filtered off and the solution acidified with hydrochloric acid. The precipitated sulphides may be examined for tin and antimony or added to the remainder of the sulphides of the sub-group.

If considerable tin is present in the alloy, it may be more advantageous to dissolve it by the following procedure. One gram of the alloy which has been cut into small shavings with a clean knife or otherwise powdered is placed in a beaker and 15 cc. concentrated hydrochloric acid added. The beaker is warmed on the water bath, one drop of concentrated nitric acid is added and the heating continued. When the action again ceases, another drop of nitric acid is added. This is repeated several times until the alloy is completely dissolved. By this process all metals in the alloy are converted into chlorides. Some of these chlorides, especially lead chloride, are insoluble in hydrochloric acid and remain as a white crystalline deposit. The tin is converted into stannic chloride and remains in solution

unless too much nitric acid has been added, which converts the tin into the insoluble metastannic acid.

The solution is diluted with an equal volume of water and the insoluble chlorides of the first group filtered off and analyzed in the usual manner. The remaining metals are tested for in the filtrate, as usual. This solution may be turbid, especially when cold, due to the action of water on $SbCl_3$. H_2S is passed without filtering as the precipitate is readily converted into the sulphide.

B.—The Residue Insoluble in Nitric Acid.

This may contain gold and platinum in their metallic forms, and tin * and antimony * in the form of metastannic and antimonic acids. The separation of the two former from the two latter depends upon the fact that the metastannic and antimonic acids are soluble in hydrochloric acid, forming $SnCl_4$ and $SbCl_5$.

Digest, therefore, the well-washed residue in concentrated hydrochloric acid at a boiling temperature for from 5 to 10 minutes: then add at once an equal volume of water (to dissolve the stannic chloride), and bring to the boiling point.

If gold or platinum existed in the original metal or alloy it will now be found in the form of a dark-brown or black powder or mass, insoluble in the hydrochloric acid. If such a residue exists, *decant while hot*, again add hydrochloric acid, heat, and again *decant*.

The Hydrochloric Acid Solution.

This solution may have a turbid appearance, especially when cold, due to the action of the water upon the $SbCl_5$; but without filtering proceed with the separation and detection of the tin and antimony by the usual process.

The Dark-colored Residue.

Add, after washing, two volumes of hydrochloric and one of nitric acid: evaporate almost or quite to dryness, dissolve in a small quantity of water (to obtain a concentrated solution), and divide into two portions.

The gold and platinum have been dissolved by the aqua-regia formed, and now exist as auric and platinic chlorides.

First Portion—Test for Gold.

Dilute with at least ten times its bulk of water: add a drop or two of a mixture of stannous and stannic chlorides; a purple or brownish-red precipitate (or coloration), purple of Cassius, constitutes the test for gold.

A convenient way of preparing this mixture of stannous and stannic chlorides is to

(*a*) Add a few drops of chlorine-water to a solution of stannous chloride; or

(*b*) Add to a small quantity of stannous chloride enough ferric chloride to produce a faint coloration.

Second Portion—Test for Platinum.

Add, without dilution, an equal volume of a strong solution of ammonium chloride. The formation, either at first or on standing, of a lemon-yellow crystalline precipitate, consisting of the double chloride of platinum and ammonium, $(NH_4Cl)_2PtCl_4$, constitutes the test for platinum.

Addition of alcohol favors the precipitation.

If the proportion of platinum is very small, the mixture, after ammonium chloride has been added, should be evaporated to dryness on a water-bath and the residue treated with dilute alcohol. The ammonium platinic chloride remains behind as a yellow crystalline powder.

* Traces may sometimes be dissolved.

SEPARATION OF THE ACIDS FROM THE BASES.

§304. The preliminary examination of **the solid material in the dry way** will give indications drawing attention to certain acids. Solutions can be evaporated to obtain a residue for this examination. Thus, *detonation* (not the decrepitation caused by water in crystals) indicates **chlorates, nitrates**, bromates, iodates. *Explosion* or *deflagration* will occur if these, or other oxygen-furnishing salts—as permanganates, chromates—are in mixture with easily combustible matter (§273, 7). Hypophosphites, heated alone, deflagrate intensely. A *brownish-yellow vapor* indicates **nitrates** or nitrites (§241, 7); a *green flame*, **borates** (§221, 7). The *odor of burning sulphur*: **sulphides**, sulphites, thiosulphates, or free sulphur. The separation of *carbon black*: an organic acid. The formation of a *silver stain*: a *sulphur* **compound** (§266, 7).

§305. When **dissolving a solid** by acids for work in the wet way, indications of the more volatile acids will be obtained. Sudden *effervescence*: a **carbonate** (oxalate or cyanate, §228, 6). *Greenish-yellow vapors*: a **chlorate** (§272). *Brownish-yellow*, chlornitrous vapors on addition of hydrochloric acid: a **nitrate**. The *characteristic odors*: salts of hydrosulphuric acid, sulphurous acid, hydrobromic acid, hydriodic acid, hydrocyanic acid, acetic acid. The separation of *sulphur*: a higher **sulphide**, etc. It will be remembered that chlorine results from action of manganese dioxide, and numerous oxidizing agents, upon hydrochloric acid.

§306. **If the material is in solution**, the bases will be first determined. (Certain volatile acids will be detected in the first-group acidulation—by indications mentioned in the preceding paragraph.) Now, it should first be considered, what acids *can be present in solution with the bases found?* Thus, if *barium* be among the bases, we need not look for *sulphuric acid*, nor, in a solution not acid, for *phosphoric acid*.

§307. As a general rule, the **non-alkali metals must be removed** from a solution before testing it for acids, unless it can be *clearly* seen that they will not interfere with the tests to be made.

Metals need to be removed: because, firstly, *in the testing for acids by precipitation*, a precipitate may be obtained from the action of the reagent on the base of the solution tested, thus: if the solution contain silver, we cannot test it for sulphuric acid by use of barium chloride (and we are restricted to use of barium nitrate). And, secondly, *in testing for acids by transposition with a stronger acid*—the preliminary examination for acids—certain bases do not permit transposition. Thus, chlorides, etc., of lead, silver, mercury, tin and antimony, and sulphide of arsenic, are not transposed by sulphuric acid, or not promptly.

§308. *If neither arsenic nor antimony* is among the bases, they may all be removed by *boiling with slight excess* of sodium or potassium carbonate, and filtering. *Arsenic and antimony*, and all other bases of the second group, may be removed by warming with **hydrosulphuric acid**, and filtering. When the bases are removed by sodium or potassium carbonate, the filtrate *must be exactly neutralized* by nitric acid, with the *expulsion of all carbonic acid* by boiling. Then, for nitric acid, the original substance may be tested.

§309. The separation of **phosphoric** acid from bases is a part of the work of the third group of metals, and is explained in §§**152** and **153**. For removal of **boric** acid, see §221; **oxalic** acid, §151; and **silicic** acid, §249, 6 and 8.

The **non-volatile cyanogen acids** can be separated from bases by digesting with potassium or sodium hydroxide (not too strong, §§**231** and **232**), adding potassium or sodium carbonate and digesting, and then filtering. The residue is examined for bases, by the usual systematic process. The solution will contain the alkali salts of the cyanogen acids, and may contain metals whose hydroxides or carbonates are soluble in fixed alkali hydroxides.

§310. PRELIMINARY EXAMINATION OF SOLIDS.

Note physical properties, such as Structure, Gravity, Color, Odor, etc.

I. Heat a portion, finely pulverized in a Dry Glass Tube closed at one end (§294).

1. *The substance suffers no change:*

Absence of volatile bodies (including combined water), of organic compounds, and of those which change color on heating.

2. *The substance changes color:*

Organic compounds *blacken* from separation of carbon, which burns.

Cu and **Co** salts *blacken* at high heat.

ZnO and most **Zn** salts, *yellow while hot, white when cold.*

PbO and **Pb** salts, *yellow while hot, yellow when cold.*

Bi_2O_3 (pale yellow) and many **Bi** salts, *orange to red-brown while hot, pale-yellow when cold.*

Fe_2O_3, and salts, *red to black while hot, reddish-brown when cold.*

$Cd(OH)_2$ and many **Cd** salts, *brown while hot, brown when cold.*

SnO_2, *brown while hot, yellow when cold.*

3. *The substance fuses:*

Most **alkali salts** and numerous other salts. Many salts dissolve in their water of crystallization when heated, becoming solid again by vaporization.

4. *The substance sublimes*, partially or wholly:

H_2O of crystallization, combination, or absorption.

Sublimate condensing in cold part of the tube.

Hg (§58, 7), *gray*, easily rubbed to globules.

$HgCl_2$ first melts, then forms *white* crystalline sublimate.

Hg_2Cl_2, without melting, forms a sublimate, *yellow while hot, white when cold.*

HgS, a *black* sublimate, turning red on trituration.

As, *steel-gray* sublimate; *garlic odor.*

As_2O_3 sublimes in *white* octahedral crystals, does not fuse (§69, 7). Garlic odor.

As_2S_3, sublimate nearly *black while hot, reddish-yellow when cold.* Garlic odor.

Sb_2S_3 fuses yellow; forms *white*, amorphous sublimates.

NH_4 salts, those not decomposing, *white* sublimate (§207, 7).
$FeCl_3$ slowly sublimes as a reddish-yellow stain (§126, 7).
S, free or by reduction of sulphide, gives reddish-brown drops, yellow when solidified.
$H_2C_2O_4$, a heavy white vapor and *crystalline* sublimate.
I, a violet vapor and *blue-black* sublimate.

5. *The substance evolves a gas or vapor:*

O indicates the presence of a **nitrate, chlorate, bromate, iodate** or **peroxide.** A small piece of coal placed upon the assay glows upon being heated.
H_2S, from hydrated **sulphides** and some **sulphites,** blackens *lead-paper.* Recognized by its odor.
SO_2, from **sulphites, thiosulphates,** certain **sulphates,** etc. Recognized by its odor and bleaching effect.
NH_3, from its compounds which decompose, *characteristic odor,* and alkaline *reaction on litmus.*
CN, recognized by characteristic *odor* and violet *flame.* Intensely poisonous.
Oxides of Nitrogen, from **nitrates** or **nitrites,** *reddish-brown, acrid vapor.*
Acetone, from **acetates,** characteristic fragrant odor.

II. Heat in a Glass Tube open at both ends (§295).

Certain of the changes stated above as occurring in operation I. are modified by oxidation. Oxides are obtained from metals, except from **Ag**, **Au** and **Pt**.
S and **sulphides** yield SO_2. Recognized by its odor and action on litmus-paper.
As yields a sublimate of As_2O_3. Garlic odor.
Sb yields a sublimate (white), of Sb_2O_3 and Sb_2O_5.
Bi, a sublimate, dark-brown while hot, lemon-yellow when cold (Bi_2O_3).
Te, gray sublimate of **tellurous anhydride** (TeO_2).
Se and **selenides** evolve SeO_2, odor resembling that of rotten horse-radish (§113).
Hg, sublimate of metallic mercury.

III. Heat in the Blowpipe Flame on Charcoal (§296).

1. *The substance decrepitates:*

Crystals as **NaCl.** (If finely pulverized, the decrepitation is avoided.)

2. *The substance deflagrates:*

Nitrates, Chlorates, Iodates, Hypophosphites, Permanganates, etc.

3. *The substance fuses, and is absorbed by the charcoal:*
   Salts of alkalis and some salts of alkaline earths.

4. *The substance is infusible and incandescent:*
   Ba , **Sr** , **Ca** , **Mg**, the residue is alkaline to test-paper.
   Al_2O_3 , **MgO** , **ZnO** (yellow while hot), not alkaline to test-paper.

5. *The substance forms an incrustation on charcoal:*
   Pb , *lemon-yellow while hot*, sulphur-yellow when cold. In thin layers, bluish-white, volatile with bluish flame.
   Bi , dark *orange-yellow while hot*, lemon-yellow when cold.
   Zn , *yellow while hot*, white when cold, greenish-white flame.
   Cd , *red-brown*, volatile, dark-yellow flame.
   As , *white*. Readily volatilized, distant from the assay, faint blue flame.
   Sb , *white*, pale-green flame.
   Sn , *faint yellow while hot*, white when cold.

6. *A metallic bead is formed:* **Pb** , **Ag** , **Au** , **Cu** , **Bi** .

IV. The Substance (or incrustation of Test III., 5) **is moistened with solution of Cobalt Nitrate and strongly ignited** (§297).

1. *The mass or incrustation is colored:*
   ZnO , *yellowish-green.*
   SnO , *bluish-green.*
   Sb_2O_5 , *dirty dark-green.*
   Al_2O_3 , **SiO_2** , phosphates, *blue.*
   MgO , *flesh-color* or *pink.*
   BaO , *brick-red.*
   SrO , **CaO** , *gray.*

V. Heat with Na_2CO_3 , on charcoal in the inner Blow-pipe Flame (§298).

1. *Metallic grains are obtained:*
   Bi , **Sb** , *brittle.*
   Pb , **Cu** , **Sn** , **Au** , *malleable.*

2. *An infusible magnetic powder is obtained:*
   Fe , **Ni** , **Co** .

VI. Heated in the Blow-pipe Flame, or in the Bunsen Flame on Charcoal, or in a loop of platinum wire (§299).

1. *The substance colors the outer flame:*

(If Test V. does not reduce metal, heat *on platinum wire* for flame color, before the blow-pipe or in Bunsen's flame.)

Yellow: **Na** and its salts, even in small quantities, impart an intense reddish-yellow.

Other salts, even in large quantities, do not interfere with this reaction; viewed through a green glass, appears orange-yellow; moistened with sulphuric acid, the test is more delicate (§206, 7).

Violet: **K** and most of its salts, except borates, phosphates and silicates, give bluish-violet flame, distinguished in presence of very small quantities of sodium compounds. Excess of the latter prevents the reaction; **Li** also masks the reaction. In presence of sodium, the potassium flame appears reddish-violet when viewed through a blue glass (§205, 7).

Red: **Ca** and its compounds produce a yellowish-red flame (§188, 7).

Sr and many of its salts yield a crimson flame, masked by much **Ba** (§187, 7).

Li and its salts produce a carmine-red flame (§210, 7). Sodium interferes with the reaction; potassium does not.

Green: Yellowish-green, **Ba** and most of its salts. Also, **Mo** and its compounds.

Emerald-green, **Cu** and most of its compounds.

Bluish-green, B_2O_3.

Yellowish-green, B_2O_3, best obtained by the addition of sulphuric acid. Heat on platinum wire until the sulphuric acid is expelled, then moisten with glycerine and ignite (§221, 7).

Whitish-green, **Zn**.

Blue: Light blue, **As** and many arsenic compounds.

Azure-blue, **Pb**, **Se**. Also, $CuCl_2$.

Greenish-blue, **Sb**, $CuBr_2$.

§311. BEHAVIOR OF SUBSTANCES BEFORE THE BLOW-PIPE WITH MICROCOSMIC SALT AND BORAX.

A clear bead is formed by fusing the flux on a loop of platinum wire. Dip the bead in the finely powdered substance to be examined, and heat again—first in the oxidizing flame; second in the reducing or inner flame. Metallic salts are mostly changed to oxides. **In the Table**—*h.* signifies hot; *c.*, cold; *sups.*, supersaturated with oxide; *s. s.*, strongly saturated; *h. c.*, hot and cold.

Color of the Bead.	With Microcosmic Salt, Sodium Ammonium Hydrogen Phosphate.		With Sodium Tetraborate (Borax).	
	In outer or oxidizing Flame.	*In inner or reducing Flame.*	*In outer or oxidizing Flame.*	*In inner or reducing Flame.*
Colorless.	**Si** (swims undissolved). **Al, Mg, Ca, Sr, Ba, Sn** (*s. s., opaque*). **Ti, Zn, Cd, Pb, Bi, Sb** (*not sat.*).	**Si** (swims undissolved). **Al, Mg, Ca, Sr, Ba** (*sups. not clear*). **Ce, Mn, Sn.**	*h. c.*: **Si, Al, Sn** (*sups. opaque*). **Al, Mg, Sr, Ca, Ba, Ag** (*not sat.*). **Zn, Cd, Pb, Bi, Sb, Ti, Mo.**	**Si, Al, Sn** (*s. s. opaque*). Alkaline earths and earths. *h. c.*: **Mn, Ce.** *h.*: **Cu.**
Yellow or Brownish.	*h.* (*s. s.*): **Fe, U, Ce.** *c.*: **Ni.**	*h.*: **Fe, Ti.** *c.*: **Ni.**	*h., not sat.*: **Fe, U.** *h., sups.*: **Pb, Bi, Sb.**	*h.*: **Ti, Mo.**
Red.	*h.* (*s. s.*): **Fe, Ni, Cr, Ce.**	*c.*: **Cu.** *h.*: **Ni, Ti** with **Fe.**	*h.*: **Fe, Ce.** *c.*: **Ni.**	*c.*: **Cu** (*sups. opaque*).
Violet or Amethyst.	*h. c.*: **Mn.**	*c.*: **Ti.**	*h. c.*: **Mn.** *h.*: **Ni** with **Co.**	*c.*: **Ti.**
Blue.	*h. c.*: **Co.** *c.*: **Cu.**	*h. c.*: **Co.** *c.*: **W.**	*h. c.*: **Co.** *c.*: **Cu.**	*h. c.*: **Co.**
Green.	*h.*: **Cu, Mo; Fe** with **Co** or **Cu.** *c.*: **Cr.**	*c.*: **Cr.** *h.*: **U, Mo.**	*c.*: **Cr.** *h.*: **Cu, Fe** with **Co.**	**Cr.** *sups.*: **Fe.**
Gray and Opaque.		**Ag, Pb, Sb, Cd, Bi, Zn, Ni.**		The same as with microcosmic salt.

§312. Grouping of the Metals. *Remove each group before testing for the next* (§63, 3).

Add hydrochloric acid, a drop at a time, as long as a precipitate is produced; agitate, and filter, §61.

Precipitate:

First Group.

Lead, §§57, 65.
$PbCl_2$ .....*white.*
Mercury, §§58, 67.
HgCl .....*white.*
Silver, §§59, 68.
AgCl..... *white.*
See §63, 6 for ambiguous results.

Pass **hydrosulphuric acid gas** into the filtrate until the solution is saturated; warm and filter, §80.

Precipitate:

Second Group.

Separate the precipitated sulphides into *two* portions by warm *digestion* with **yellow ammonium sulphide.**

Arsenic, §§69, 85, 87, 88.
As_2S_3 and **As_2S_5** *yellow.*
Antimony, §§70, 85, 89.
Sb_2S_3 and **Sb_2S_5** *orange.*
Tin, §§71, 85, 90, 92.
SnS ..... *brown.*
SnS_2 ..... *yellow.*
Gold, §§73, 93.
Au_2S_3 .....*yellow.*
Platinum, §§74, 94.
PtS_2.....*black.*
Molybdenum §§ 75, 91.
MoS_3 ....*brown.*

Mercury, §§58, 95, 96.
HgS .....*black.*
Lead, §§57, 98.
PbS.....*black.*
Bismuth, §§76, 100.
Bi_2S_3..... *black.*
Copper, §§77, 102.
CuS..... .....*black.*
Cadmium, §§78, 102.
CdS .....*yellow.*
Rare metals, §§104 to 113.

Boil the filtrate, add a few drops of **nitric acid,** *boil,* add **ammonium chloride** and **ammonium hydroxide,** §127.
(If *phosphates* or *oxalates* may be present follow the text as given in §§145 to 153.)

Precipitate:

Third Group.

Aluminum, §§124, 130.
$Al(OH)_3$..... *white. gelatinous.*
Chromium §§125, 130.
$Cr(OH)_3$ ..*bluish-green.*
Iron, §§126, 128, 130.
$Fe(OH)_3$ *reddish-brown.*

Rare metals of the Third and Fourth Groups, §§154 to 174.

Pass **hydrosulphuric acid gas** into the **ammoniacal** filtrate until no further precipitate is formed, §137.

Precipitate:

Fourth Group.

Cobalt, §§132, 138, 140.
CoS.....*black.*
Nickel, §§133, 140.
NiS..... .*black.*
Manganese, §§134, 142.
MnS..... *flesh-colored.*
Zinc, §§135, 142, 143.
ZnS..... *white.*

To the *filtrate* add **ammonium hydroxide** and **ammonium carbonate,** warm gently and filter. To a portion of the *filtrate* add **sodium phosphate,** §190.

First Precipitate, **$BaCO_3$, $SrCO_3$, $CaCO_3$.**

Second Precipitate, **$MgNH_4PO_4$.**

Fifth Group.

Barium, §§186, 191.
$BaCO_3$..... *white.*
Strontium §§187, 191.
$SrCO_3$ ..... *white.*
Calcium, §§188, 191.
$CaCO_3$..... . *white.*
Magnesium, §§189, 193.
$MgNH_4PO_4$..... *white.*

Not precipitated by the above **group reagents,** §211.

Sixth Group.

Potassium, §§205, 212.
Sodium, §§206, 212.
Ammonium, §§207, 213.
Caesium, §208.
Rubidium, §209.
Lithium, §210.

§313. Table for Review

Neutral or slightly acid solutions of the salts of

Pb	(1) Silver Group.	$PbCl_2$	Add hot water.	$PbCl_2$	$H_2SO_4 = PbSO_4$ White.				
					$H_2S = PbS$ Black.				
					$K_2CrO_4 = PbCrO_4$ Yellow.				
					$KI = PbI_2$ Yellow.				
Hg′		HgCl		HgCl	Add NH_4OH	$NH_2HgCl + Hg$ Black.			
Ag		AgCl		AgCl		$(NH_3)_3(AgCl)_2$	Add HNO_3	AgCl White.	
As‴	Add hydrochloric acid.	Solutions not precipitated. Pass hydrosulphuric acid gas into the warm solution.	(2) Tin and Copper Group	As_2S_3	Add yellow ammonium sulphide.	$(NH_4)_4As_2S_5$	Add dilute hydrochloric acid.	Division A. Tin Group.	Dissolve in HCl with the aid of $KClO_3$.	H_3AsO_4	Transfer a portion of the solution to the Marsh apparatus.
As^{v}				As_2S_5		$(NH_4)_3AsS_4$		As_2S_5		.....	
Sb^{v}				Sb_2S_5		$(NH_4)_3SbS_4$		Sb_2S_5		$SbCl_5$	
Sb‴				Sb_2S_3		.....		.....		.....	
Sn^{iv}				SnS_2		$(NH_4)_2SnS_3$		SnS_2		$SnCl_4$	
Sn″				SnS		.....		.....		.....	
Au‴				Au_2S_3		Solution.		Au_2S_3		$AuCl_3$	
Pt^{iv}				PtS_2		Solution.		PtS_2		$PtCl_4$	
Mo^{vi}				MoS_3		$(NH_4)_2MoS_4$		MoS_3		$MoCl_6$	
Hg″				HgS	Division B. Copper Group.	HgS	Digest in hot dilute HNO_3.	HgS	Dissolve in nitrohydroch		
Pb				PbS		PbS		$Pb(NO_3)_2$	Add two or three drops of dilute H_2SO_4	$PbSO_4$ Confir	
Bi				Bi_2S_3		Bi_2S_3		$Bi(NO_3)_3$		$Bi(NO_3)_3$	Add NH_4OH
Cu′				Cu_2S		Cu_2S		$Cu(NO_3)_2$		$Cu(NO_3)_2$	
Cu″				CuS		CuS		.....		.....	
Cd				CdS		CdS		$Cd(NO_3)_2$		$Cd(NO_3)_2$	
Al			Solutions not precipitated. Cr^{vi} becomes Cr''', Fe''' becomes Fe'' and Mn^{vii} becomes Mn''. Boil to expel H_2S, add HNO_3 and boil to oxidize ferrosum; and add ammonium chloride and ammonium hydroxide.	(3) Iron Group.	$Al(OH)_3$	Boil with NaOH.	$NaAlO_2$	Add NH_4Cl or render a		
Cr‴ Cr^{vi}				$Cr(OH)_3$		$Cr(OH)_3$		Fuse on platinum foil with KNO_3 and Na_2CO_3			
Fe″ Fe‴				$Fe(OH)_3$		$Fe(OH)_3$					
Co				Solutions not precipitated. $MnCl_2.2NH_4Cl$, $(NH_4)_2ZnO_2$, and $MgCl_2$. NH_4Cl are formed; also soluble double compounds of Co and Ni with ammonium hydroxide. Add hydrosulphuric acid to the strongly ammoniacal solutions.	(4) Zinc Group.	CoS	Digest with cold dilute HCl.	CoS	Dissolve in nitrohydro-
Ni						NiS		NiS			
Mn″ Mn^{vii}						MnS		$MnCl_2$	Boil, cool, add excess	
Zn						ZnS		$ZnCl_2$			
Ba						Solutions not precipitated. Add NH_4OH and $(NH_4)_2CO_3$.	(5) Calcium Group.	Division A.	$BaCO_3$	Dissolve in $HC_2H_3O_2$. Add	
Sr									$SrCO_3$		
Ca									$CaCO_3$		
Mg								Solutions not precipitated. Add Na_2HPO_4 to a portion, and if a precipitate is obtained, use $(NH_4)_2HPO_4$ with the other portion, §211, or follow §212.			
K											
Na											
NH_4											

SEPARATIONS OF THE METALS.

sH_3	Conduct the gas into $AgNO_3$ solution. Also obtain mirror and spots.	H_3AsO_3	Remove $AgNO_3$ with $CaCl_2$ and add H_2S		As_2S_3	Lemon yellow.
.....						
$_3$ and Sb		$SbAg_3$	Dissolve in hot HCl, dilute, filter and add H_2S		Sb_2S_3	Orange.
.....						
n	Digest with warm HCl.	$SnCl_2$	Test with $HgCl_2$.		HgCl, White; or Hg Gray.	
.....		Sb	Dissolve in nitro-hydrochloric acid.	$SbCl_5$	Boil with solution of $FeSO_4$.	$SbCl_5$ reject or test in Marsh apparatus.
u		Au		$AuCl_3$		Au — Dissolve in nitrohydrochloric acid, evaporate to dryness with excess of NH_4Cl and digest with alcohol. — $AuCl_3.NH_4Cl$ Evaporate and ignite to Au°, Yellow.
t		Pt		$PtCl_4$		Pt — $(NH_4)_2PtCl_6$ Ignite to Pt°, Gray.
to green- n or black lution.	Evaporate to dryness with excess of HNO_3. Dissolve residue in NH_4OH and add to an excess of HCl. Test this solution with Na_2HPO_4					Ammonium phosphomolybdate, Yellow.

d and test with $SnCl_2$ and Cu wire.

mation of PbI_2 or $PbCrO_4$.

$H)_3$ Add hot K_2SnO_2 } Bi° Black.

$H)_2.2NH_4OH.2NH_4NO_3$ } Deep blue solution evidence of copper. For traces add $HC_2H_3O_2$ and test with $K_4Fe(CN)_6$ { $Cu_2Fe(CN)_6$ Red-brown.

.....

$H)_2 2NH_4OH.2NH_4NO_3$ } Add KCN till blue color disappears, then H_2S { CdS Lemon-yellow.

HCl and precipitate with $(NH_4)_2CO_3$ { $Al(OH)_3$ White, gelatinous.

Acidify with $HC_2H_3O_2$ and add $Pb(C_2H_3O_2)_2$ { $PbCrO_4$ Lemon-yellow.

Dissolve in HCl and add KCNS { $Fe(CNS)_3$ Blood red.

Test original solution (acid) with KCNS for Fe''' and with $K_3Fe(CN)_6$ for Fe'' { $Fe_3[Fe(CN)_6]_2$ Blue.

[a. Test with borax bead. Blue bead. b. Add $NaHCO_3$ and H_2O_2, Green solution.] Or add nitroso-β naphthol. Co—Red precipitate. } Test with borax bead.

[a. Test with borax bead. Brown bead. b. Heat with Br and NaOH { $Ni(OH)_3$ } add KI. Free I in CS_2] Ni— Solution. } Add NH_4OH filter and add H_2S { NiS, Black

$)_2$ } Boil with PbO_2 and HNO_3 } $HMnO_4$ Purple.

O_2 } Add H_2S } ZnS White.

Dissolve in HCl and add H_2SO_4 { $BaSO_4$ White.

$_3O_2)_2$	Add NH_4OH and $(NH_4)_2CO_3$.	$SrCO_3$	Dissolve in $HC_2H_3O_2$	$Sr(C_2H_3O_2)_2$	Divide into two portions: 1. Add $CaSO_4$, set aside ten minutes { $SrSO_4$, White. Moisten $SrSO_4$ with HCl and apply flame test.
$H_3O_2)_2$		$CaCO_3$		$Ca(C_2H_3O_2)_2$	2. Add K_2SO_4, boil, set aside ten minutes. Filter and add $NH_4)_2C_2O_4$ { CaC_2O_4, White, soluble in HCl.

H_4PO_4, White.

—Apply flame test using cobalt glass. Violet.

—After removal of Mg apply flame test, yellow.

H_4—To the original solution add KOH in strong excess, warm (note odor) and test with moist litmus paper; pass gas into Nessler's reagent { NHg_2I, Brown.

§314. Table I.—Preliminary Examination for Acids.

By use of sulphuric acid, etc.

Concerning the indications of acids in the Blow-pipe Examination, see §§304 and 310; the indications in dissolving Solids, see §305; the considerations relative to any bases already determined, see §306; the Removal of Bases, see §309; Reactions in the Wet way, see §§315-317.

Unless otherwise directed, to a little of the solid substance or residue by evaporation, or very concentrated solution, in a test-tube, add a little concentrated sulphuric acid, and heat gently, not enough to vaporize the sulphuric acid.* *Results as follows:*

Borates.	All borates are transposed by sulphuric acid, dilute or concentrated, the boric acid not being volatilized. Non-alkali borates not entirely insoluble in water. Readily transposed by nearly all acids. The free acid is soluble in alcohol, which solution burns with a *green flame* (§221, 8). Alkali borates fuse to a clear glassy bead on a loop of platinum wire (§221, 7).
Acetates.	Transposed by sulphuric acid, may be distilled from the dilute acid without decomposition, with the concentrated acid partial decomposition occurs, leaving a carbonaceous residue. **Acetic acid, $HC_2H_3O_2$**, *odor of vinegar*. Digested with alcohol and sulphuric acid, gives *odor of acetic ether* (§223, 1). Acetates are transposed by hydrochloric and nitric acids. In solution form no precipitates, but give red solution with ferric salts (§152). Acetates when heated with arsenous oxide evolve *cacodyl oxide*, $As_2(CH_3)_4O$, poisonous, having a stupefying odor.
Citrates and **Tartrates.**	Transposed by dilute, charred when heated with concentrated sulphuric acid, with evolution of CO_2; does not distinguish from other organic compounds. Study §§224 and 225.

*In presence of many free metals as **Mg, Fe, Cu**, etc., the concentrated sulphuric acid is decomposed with evolution of sulphur dioxide; this if passed into calcium hydroxide solution gives a precipitate of calcium sulphite which the student will mistake for a carbonate. With dilute sulphuric acid many of the metals give a rapid generation of hydrogen; this gives no precipitate when passed into a solution of calcium hydroxide, but the student is liable to mistake the evolution of the hydrogen for effervescence of a carbonate.

Oxalates. Decomposed with evolution of CO_2 and **CO**, the latter burning with a pale-blue flame (§**227**, 7). Pass the evolved gases into a solution of calcium hydroxide, obtaining a precipitate of calcium carbonate (§**228**, 8). Or warm original solution with dilute H_2SO_4 and $KMnO_4$, if not decolored $H_2C_2O_4$ is absent, but if decolored, pass the evolved gas into $Ca(OH)_2$, and if a precipitate is formed the proof is absolute in absence of other organic matter: $2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$. $CO_2 + Ca(OH)_2 = CaCO_3 + H_2O$. The free acid or the soluble salts are precipitated by $CaCl_2$, soluble in **HCl**, insoluble in $HC_2H_3O_2$ (§§**315** and **317**). Dilute sulphuric acid transposes all oxalates, but decomposes none. (In the above tests barium hydroxide may, with advantage, be substituted for the more dilute calcium hydroxide.)

Carbonates. *Use the dilute acid.* **Carbonic anhydride, CO_2.** Gas obtained with sudden effervescence, colorless and odorless, feebly reddening litmus and making solution of calcium hydroxide turbid (§**188**, 8). In the presence of the fixed alkali *bicarbonates* or with excess of CO_2, considerable quantities of **Ba**, **Sr**, **Ca**, and **Mg** may be held in solution (§**189**, 5*c*); but not more than traces of metals of the first four groups can be present. With solutions of the *normal* fixed alkali carbonates, other metals cannot be present.

Cyanides. Most cyanides are transposed by dilute sulphuric acid, all of them by the hot concentrated acid with evolution of hydrocyanic acid, **HCN**. *Poisonous* gas with *peach-blossom odor.* The *gas* precipitates silver nitrate on a glass rod, as **AgCN**. Change to thiocyanate and obtain the blood-red color with ferric salts (§**230**). Change to ferrocyanide and obtain the blue precipitate with iron salts (§**231**). Alkali cyanides are decomposed by all acids. In solution they precipitate most of the metals of the second, third and fourth groups (§**230**).

Ferrocyanides. Ferricyanides. Thiocyanates. Evolve **HCN** when heated with dilute sulphuric acid (§**231**), carbon monoxide when heated with the concentrated acid. The insoluble salts of $H_4Fe(CN)_6$ and $H_3Fe(CN)_6$ are transposed when boiled with **KOH**, and after filtering and acidifying may be tested with iron salts (§**126**, 6*b*).

TABLE I.—*Continued.*

	The cyanogen of single cyanides is separated by slightly acidulating, adding calcium carbonate and distilling—*ferrocyanogen*, *ferricyanogen* and *thiocyanogen* being retained as salts. **Thiocyanates** when fused with potassium nitrate form soluble sulphates.
Cyanates.	Sulphuric acid decomposes cyanates with evolution of CO_2 (§**233**).
Nitrites.	**Nitrous acid, HNO_2**, and **nitric peroxide, NO_2**, characteristic odor. Color red-brown. Immediate reaction with potassium iodide and starch, or with carbon disulphide and potassium iodide from dilute solutions of the acid or from the salts after acidifying with acetic acid (§**239**, 6*B*).
Nitrates.	**Nitric acid, HNO_3**. If reducing agents be present the brown nitric oxide is evolved. Boil five or ten cubic centimeters of reagent hydrochloric acid with sufficient indigo solution to give a decided blue color and then add a small portion of the solution to be tested (bases should have been removed previously). *Failure to decolor the indigo solution* indicates **absence** of nitrates. Test for the *brown ring* (§**241**, 8*a*). Test with *diphenylamine solution* (§**241**, 8*f*). Test by *reduction to nitrite* with potassium hydroxide and aluminum wire (§**241**, 8*e*). Test by *reduction to* **NH_3** and identify with Nessler's reagent (§**241**, 8*d*). Test for a *yellow ring* with sodium salicylate and concentrated sulphuric acid (§**241**, 8*c*).
Fluorides.	**Hydrofluoric acid, HF**. Warm in a lead dish with concentrated sulphuric acid and observe the etching effect on a glass plate (§**246**). Decompose by warming with sulphuric acid and sand, and pass the evolved **SiF_4** into water. Fluosilicic acid is formed with precipitation of **SiO_2** (§**246**, footnote).

Fluosilicates. Decomposed by heating with concentrated sulphuric acid with evolution of **HF**. By heat alone they are decomposed into fluorides and silicon fluoride, SiF_4 (§247).

Silicates. Soluble silicates are transposed by acids with formation of a gelatinous precipitate of **silicic acid,** H_2SiO_3 (non-volatile). Insoluble silicates are fused with alkali carbonates, forming soluble alkali silicates. Filter, evaporate the filtrate to dryness and re-evaporate with an excess of hydrochloric acid. The silicates are all changed to silica, SiO_2, and may be further identified by volatilization as SiF_4 (§249, 6, 7 and 8). Also confirm by the bead test (§249, 7).

Hypophosphites. All hypophosphites are soluble in water. Sulphuric acid is reduced to sulphurous acid and then to sulphur. Hypophosphorous acid is a very powerful reducing agent (§252, 6). Upon heating, phosphoric acid or phosphates are formed with evolution of *phosphine* (§252, 7).

Phosphates. **Phosphoric acid,** H_3PO_4. Changed by ignition to HPO_3, which sublimes undecomposed (§255, 7). Dilute sulphuric acid transposes all phosphates, but phosphoric acid displaces sulphuric acid from all sulphates upon heating above the boiling point of sulphuric acid. The sulphuric acid is vaporized, the reaction being slow with barium sulphate (§255, 6*B*).

The phosphates present considerable difficulty in the separations of the metals. See §§145-153. The acid is detected by the reaction with ammonium molybdate; arsenic acid should not be present (§§75, 4*d*; 255, 8; 315).

Sulphides. Most sulphides are transposed by dilute sulphuric or hydrochloric acid with formation of the *gaseous hydrosulphuric acid,* H_2S, colorless, having an *odor of rotten eggs.* The gas blackens paper wet with solution of lead acetate. Concentrated sulphuric acid, nitric acid or chlorine decomposes sulphides with separation of sulphur. The gas, H_2S, passed into ammonium hydroxide gives a beautiful violet color with sodium nitroferricyanide (§257, 8*d* and *f*). The hydrosulphuric acid gas and the sulphur burn with a pale blue flame, evolving fumes of SO_2.

TABLE I.—*Continued.*

Sulphites.	**Sulphurous anhydride, SO_2.** *Odor of burning sulphur.* Bleaches litmus. Colors iodic acid and starch (§**265**, 8). Sulphites precipitate salts of all non-alkali bases. See §**265**, 6*A* and *B*.
Thiosulphates.	Decomposed by acids with evolution of sulphurous anhydride and separation of sulphur (§**258**, 6*B*). Many thiosulphates decompose upon standing, mercury and silver thiosulphates almost instantly, a sulphide of the metal being formed.
Sulphates.	All soluble sulphates react with solutions of barium salts with formation of the insoluble barium sulphate. Insoluble sulphates are changed to soluble alkali sulphates upon fusion with fixed alkali carbonates (§§**186**, 6*e*; **266**, 6*A*; **315**; **317**).
Chlorides.	**Hydrochloric acid, HCl.** Slight effervescence. Slight, irritating odor. The *gas* forms a white precipitate (**AgCl**) with solution of silver nitrate on a glass rod; the precipitate being insoluble in dilute nitric acid but soluble in ammonium hydroxide (§**269**, 8*a*). The gas forms a white cloud with vapor of ammonia. Obtain CrO_2Cl_2 by §**269**, 8*d*.*
Chlorites.	Decomposed with evolution of chlorine; bleach indigo and decolor $KMnO_4$ (§**271**, 8).
Hypochlorites.	Decomposed with evolution of chlorine; bleach indigo (§**270**, 8) but do not decolor $KMnO_4$.
Chlorates.	Detonation with concentrated sulphuric acid: $3KClO_3 + 2H_2SO_4 = 2KHSO_4 + KClO_4 + 2ClO_2 + H_2O$. Greenish-yellow gas. *Odor of chlorine.* Bleaches litmus. Chlorates are transposed by nitric acid and decomposed by hydrochloric acid (§**259**, 6*B*5). By ignition reduce to chlorides: $2KClO_3 = 2KCl + 3O_2$. Reduce to chloride with zinc and dilute sulphuric acid: $2KClO_3 +$

* An application of the chlorochromic test (Wiley, *C. N.*, 1880, **41**, 176).

$6Zn + 7H_2SO_4 = 6ZnSO_4 + K_2SO_4 + 2HCl + 6H_2O$. Also reduce to chloride by sulphurous acid after addition of dilute sulphuric acid: $2KClO_3 + H_2SO_4 + 6H_2SO_3 = 2HCl + K_2SO_4 + 6H_2SO_4$. In each case identify the chloride * produced by precipitation with silver nitrate: $HCl + AgNO_3 = AgCl + HNO_3$. Compare §283.

Bromides. **Bromine, Br**, from decomposition of bromides. *Odor is acrid and chlorine-like.* Color slightly yellowish-brown. Decomposed by HNO_3 and by **Cl**, forming **Br**, which is detected by the solution in carbon disulphide (colors starch feebly yellow). To detect bromide in presence of iodide follow directions at §276, 8*c*. In solution give white or yellowish-white precipitates with salts of the first group bases (§276, 5). Compare reactions by aid of the table at §283. See also §§276, 8, and 316.

Bromates. Concentrated sulphuric transposes bromates, but the heat of combination, aided by the external heat directed, decomposes the bromic acid into bromine, oxygen and water, and the sulphuric acid is not reduced. With dilute sulphuric acid bromates are merely transposed, no bromine being liberated. A gradual liberation of bromine is due to the decomposition of the free bromic acid. Ignition of all bromates with an alkali carbonate forms a bromide (§278, 8).

Iodides. Most iodides are transposed by dilute sulphuric acid, hydriodic being liberated but not volatilized without partial decomposition. With the concentrated acid decomposition takes place with liberation of **iodine**. When the mixture of the iodide with sulphuric acid is warmed violet vapors are evolved. Soluble iodides are decomposed by HNO_3, **Cl** and **Br** with liberation of iodine, coloring starch blue and carbon disulphide violet. In solution give colored precipitates with salts of the first group metals (§280, 6*A*). Compare reactions by table §283. See also §§280, 8, and 316.

* If a chloride be present in original solution, it is removed by $AgNO_3$ and any of the reduction tests applied to the filtrate.

TABLE I.—*Continued.*

Iodates.	Transposed by concentrated sulphuric acid; decomposed by heat alone at 300°, **I** and **O** being liberated. Acidify and add a drop of sulphurous acid (better uric acid); test for the free iodine by shaking with carbon disulphide. Precipitated by silver nitrate and dissolved on continued heating with dilute nitric acid (separation from iodides). Compare the table at §**283.** Study §**281,** 6 and 8.
Arsenites.	Transposed to arsenous acid by nearly all acids. H_2S in acid solution forms As_2S_3 (§**69,** 6*e*). A yellow precipitate in neutral solutions with silver nitrate. Decolors a solution of potassium permanganate. Identify in second group of bases.
Arsenates.	**Arsenic acid,** H_3AsO_4, not volatilized at 338°. Readily reduced to arsenous acid by sulphurous acid; also by **HI** with separation of iodine. Does not decolor a solution of potassium permanganate. Chocolate-colored precipitate with solution of silver nitrate. Very slowly precipitated from acid solutions by hydrosulphuric acid. When slightly warmed reacts with ammonium molybdate, giving a *yellow precipitate* not readily distinguished from ammonium phosphomolybdate (§§**69,** 6*m*; **75,** 6*d* and *g*; **255,** 6*A*).
Chromates.	Transposed by dilute sulphuric acid, the hot concentrated acid liberates oxygen, forming chromic sulphate. *Red precipitate* with silver salts; *yellow precipitate* with salts of lead and barium. By reduction, changed to the green chromium salt. Alkali chromates dissolve in water to *yellow* solutions.
Dichromates.	Same as for chromates with sulphuric acid. Yellow precipitate with lead and barium salts, red with silver salts. Reduced to the green chromic salt. *Normal chromates* are more readily precipitated by solutions of the alkaline earths than are the *dichromates.* Alkali dichromates

	dissolve in water with a reddish-yellow color, changed to a bright yellow of the normal chromate by the alkalis.
Manganates.	Decomposed on warming with concentrated sulphuric acid with detonation or sudden puffing, evolving oxygen, a sulphate being formed. Solution in water *green*, rapidly turning *red* or *violet* with separation of MnO_2; fairly stable green solution in presence of an alkali. By reducing agents readily changed to colorless solution of manganous salt. Manganates are formed by fusion of a manganous salt with an oxidizer in alkaline mixture (§**134**, 7).
Permanganates.	Decomposed by hot H_2SO_4, the same as manganates. With the cold, concentrated acid a sulphate of heptad manganese is formed, green solution, $(MnO_3)_2SO_4$. Solution in water *deep-violet* color. Easily reduced to colorless manganous salt. Obtained by boiling a lower compound of manganese with nitric acid and lead peroxide (§**134**, 8).

§315. Table II.—Examination of Some Acids Precipitated by Barium and Calcium Chlorides.

Concerning the removal of basis before testing for acids see §307.

Heat a portion of the solution acidulated with* **HCl** *and add both* **$BaCl_2$** *and* **$CaCl_2$.**

A **precipitate,** *barium sulphate,*† *white,* is **proof** of the presence of **sulphates.** *Boil* the solution for two or three minutes, allow the precipitate to settle and decant through a filter. Render the filtrate *alkaline* with **NH_4OH.**

Precipitate: CaC_2O_4, $Ca_3(PO_4)_2$. Also barium and calcium salts of boric, silicic, hydrofluoric, fluosilicic, molybdic, chromic,** arsenic and iodic acids.‡ These acids will be identified by **§314,** or during the examination for bases.

Add acetic acid to a distinctly acid reaction.

Residue: CaC_2O_4 (white).	**Solution: H_3PO_4, $CaH_4(PO_4)_2$,** etc., **§255,** 5.
Dissolve in dilute **HNO_3**, add dilute **$KMnO_4$** (**§227,** 6*A*); decoloration shows that oxalic acid is present (many other organic compounds not here provided for will decolor **$KMnO_4$**).	**Add excess of ammonium molybdate;** precipitate, yellow, **§255,** 6*A*.
Study **§151, §227,** 6 and 8.	With ammonium molybdate, arsenic and phosphoric acids react similarly, except that the phosphoric acid is precipitated in the cold and the arsenic acid not until warmed to about 30° (**§69,** 6*m*).
	Study §§**145** to **153.**

* If sulphites are present, sulphur dioxide is set free and driven off as a gas upon heating; also in presence of oxidizing agents as **$KClO_3$,** oxalic acid may be decomposed and all lower oxidized sulphur compounds are oxidized to **H_2SO_4.** Consult **§265,** 6 and 8.

† Concerning the analysis of barium sulphate or other insoluble sulphates see **§266,** 8.

‡ Tellurates (**§112**), selenates (**§113**), and some of the other rarer acids are also precipitated.

** **$BaCrO_4$** or **CaC_2O_4** may be present, both cannot be (**§227,** 6*A*).

§316. Table III. Examination of Some of the Acids Precipitated by Silver Nitrate. See §§307-309.

To the neutral or slightly acid solution* add **silver nitrate.**

Precipitate: Ag_3AsO_3, Ag_3AsO_4, Ag_2CrO_4, Ag_3BO_3, $Ag_2C_4H_4O_6$, $Ag_2C_2O_4$, AgCN, $Ag_4Fe(CN)_6$, $Ag_3Fe(CN)_6$, AgCNO, AgCNS, $AgNO_2$, Ag_2SiF_6, Ag_2SiO_3, Ag_3PO_4, Ag_2S, $Ag_2S_2O_3$, Ag_2SO_3, Ag_2SO_4 AgCl, AgBr, $AgBrO_3$, AgI, $AgIO_3$, $Ag_2H_3IO_6$.

Digest with hot dilute **nitric acid.** *Filter and wash.* Reject the filtrate.

Residue: AgI, AgBr, AgCl, AgCN, AgCNS, Ag_2CrO_4†, $AgIO_3$†.

Add an excess of **ammonium hydroxide** *and warm gently.* Filter.

Residue: AgI, indicating iodides. Test the original solution for iodides, by chlorine-water with carbon disulphide or starch, § **280,** 8.

Study the text at § **280, 5** and 6 and the comparative table § **283.**

Filtrate: Ammonium silver compounds, representing **HCl, HBr, HCN, HCNS, HIO_3,**

Add dilute **HNO_3** *to a slight acidulation.*

Precipitate: AgCl, AgBr, AgCN, AgCNS, $AgIO_3$.

For **Chlorides.**	For **Bromides.**	For **Cyanides.**	For **Thiocyanates.**	For **Iodates.**
Test the original powder or solution by distillation with **$K_2Cr_2O_7$** and **H_2SO_4** (§**269,**8*d*). For detection in presence of **AgCN** and **AgCNS** see §**269,**8*e*.	Test the original solution with chlorine water and carbon disulphide (§**276,**8).	Test the original solution as directed in §**230,**6 and 8; both by formation of Prussian blue and by conversion into thiocyanate.	Acidulate the original solution and test with ferric chloride §**234,** 8. Study §**234,** 6.	Decompose the **$AgIO_3$** with **H_2S** and test the filtrate for hydriodic acid §**281,** 6*B4*. Acidify the original solution with **HCl,** add a drop of **H_2SO_3** (or better uric acid) and shake with **CS_2** (§**281,**8)

* If alkaline, the solution should be neutralized with nitric acid (use litmus or phenolphthalein as an indicator). Should effervescence result, boil until all the **CO_2** is driven off. Should a precipitate form, remove it by filtration.

† By repeated digestion with nitric acid the silver chromate and iodate may be completely dissolved.

§317. Table for Identification and Separation of the Commonly Occurring Anions (Acids).*

1. **Boil the material with dilute HNO_3.** There results:

CO_2	Effervescence; turbidity in a drop of lime-water.
SO_2	Effervescence, penetrating odor.
N_2O_3	Effervescence, red-brown fumes, odor.
H_2S	Odor, blackening of paper moistened with lead acetate, separation of sulphur in the solution.
HCN	Odor } Often masked by the others; see special tests below.
$C_2H_4O_2$	Vinegar odor }

2. **Boil with concentrated Na_2CO_3 solution**; all cathions (bases) except the alkalis are precipitated as carbonates or hydroxides and removed by filtration. The filtrate contains all the anions (acids) and the excess of CO_3''. Acidulation with HNO_3 sets free CO_2, and SiO_2 is precipitated; identified in the microcosmic salt bead. The filtrate is made ammoniacal.

3. **$Ca(NO_3)_2$ solution precipitates:**

F'	as CaF_2	insoluble in acetic acid;	dilute HCl	insoluble; H_2SO_4 liberates HF.
C_2O_4''	as CaC_2O_4			soluble, reappearing with NH_3; decolors $KMnO_4$ solution.
CN'	as $Ca(CN)_2$	soluble in acetic acid		heated with $Fe'' + Fe''' + OH'$ gives Prussian blue on acidifying.
$C_4H_4O_6''$	as $CaC_4H_4O_6$			with K' ions in concentrated solution potassium bitartrate precipitated.
$HAsO_3''$	as $CaHAsO_3$			In the filtrate from the above, H_2S precipitates As_2S_3 at once in the cold.
$HAsO_4''$	as $CaHAsO_4$			In the filtrate from the above, H_2S slowly precipitates from hot solution $S_2 + As_2S_3$.
HPO_4''	as $CaHPO_4$			In the filtrate from the above, ammonium molybdate gives yellow precipitate; or $Mg'' + NH_4' + OH'$ gives $MgNH_4PO_4$.

4. **In the filtrate from 3. $Ba(NO_3)_2$ precipitates:**

$CrO_4''(Cr_2O_7'')$ as $BaCrO_4$, yellow, soluble in HCl; the yellow color of the solution becoming green on boiling with alcohol.

* From *Chem. Prakt.* Abegg and Herz (1900), Breslau, Page 113; reviewed by Fresenius, *Z.*, 1900, **39**, 566.

SO_4'' as $BaSO_4$ ⟩ insoluble in HCl; on ignition ⟨ unchanged, remains insoluble in HCl.

SiF_6'' as $BaSiF_6$ ⟩ insoluble in HCl; on ignition ⟨ gives off SiF_4, which deposits SiO_2 in a drop of water; the residue, BaF_2, is soluble in HCl.

5. **The filtrate from 4. is exactly neutralized with HNO_3*; $Zn(NO_3)_2$ then precipitates:**

$Fe(CN)_6'''$ as $Zn_3[Fe(CN)_6]_2$ brownish-yellow ⟩ dissolved by OH' ⟨ brown coloration.

$Fe(CN)_6''''$ as $Zn_2Fe(CN)_6$ white ⟩ gives with Fe''' and H' ⟨ Prussian blue.

6. **A few drops of the filtrate from 5. are treated with as little Fe''' as possible:**

Red coloration { $Fe(CNS)_3$, $Fe(C_2H_3O_2)_3$ } on heating { permanent red color; precipitate and colorless solution.

In the absence of CNS' another drop is tested with Ag' for the halogens; if a precipitate results or if CNS' is present, *one* part of the solution is treated with CS_2 and a *little* Cl-water:

I' violet coloration, disappears with
Br' brown coloration, does not disappear with } much Cl-water.

The second portion is evaporated to dryness with $K_2Cr_2O_7$, fused, and the mass after cooling distilled with concentrated H_2SO_4; appearance of oily brown drops of CrO_2Cl_2, forming CrO_4'' with water: Cl'.

7. **A concentrated water-extract of the original substance is treated with concentrated H_2SO_4 and solid $FeSO_4$ or Fe'' solution. prepared cold;** a brown coloration shows the presence of NO_3'.

The anions mentioned above to some extent exclude one another, being unstable when together in solution owing to their power of mutual oxidation and reduction, *e. g.*, SO_3'' and S''; SO_3'' and NO_2'; NO_2' and CN'; NO_2' and S''; NO_2' and I'; NO_2' and $HAsO_3''$; S'' and $HAsO_4''$, etc. It is to be noticed that this always simplifies the analytical procedure.

§318. Notes on the Detection of Acids.

1. The precipitation of **tartrates** by calcium salts is incomplete; from calcium sulphate solution a precipitate forms slowly or not at all. Calcium tartrate is soluble in the *cold* in a solution of KOH, precipitating gelatinous on *boiling*; again soluble on *cooling* (separation from citrate). Calcium tartrate is soluble in acetic acid (separation from oxalate).

2. A number of basic **carbonates** give almost no effervescence when treated

*In the original German text it is directed to use HCl at this point.

with acids. *To detect the presence of small amounts of carbonate*, it is recommended to place the dry powder in a test-tube and fill about three-fourths full of distilled water. Close the test-tube with a two-holed rubber stopper containing a thistle tube reaching nearly to the bottom of the test tube, and a delivery tube reaching just through the stopper. Add dilute sulphuric acid and warm gently. The carbonate is decomposed, driven from the solution, and, owing to the limited air space, readily passes through the delivery tube into the solution of calcium hydroxide.

3. With the generation of an abundance of CO_2, the precipitate first formed in the $Ca(OH)_2$ is redissolved (solution of lime in spring water). Boiling drives off the excess of CO_2 and causes the reprecipitation of the $CaCO_3$. Barium hydroxide may be used instead of calcium hydroxide.

4. If compounds have been strongly ignited previous to solution for analysis, **oxalates** cannot be present.

5. In **Table II** (§315), if strong oxidizing agents are present, as $KClO_3$, $K_2Cr_2O_7$, $KMnO_4$, etc., the **oxalic acid** will be decomposed on warming with hydrochloric acid. This may be avoided by adding calcium chloride to the solution, neutral or alkaline with ammonium hydroxide. The oxalate will be precipitated and thus separated from the oxidizing agents. After filtering, the precipitate is digested with dilute acetic acid, filtered and the filtrate tested for phosphate with ammonium molybdate. The residue is dissolved in hydrochloric acid, filtered if necessary (calcium sulphate does not dissolve readily), and the filtrate made alkaline with ammonium hydroxide. The precipitate thus obtained is washed, dissolved in nitric acid and tested with potassium permanganate. The filtrate from the solution after the addition of calcium chloride is acidified with hydrochloric acid, heated to boiling and tested for sulphate by the addition of a few drops of barium chloride (§317).

6. In **Table II**, if **sulphites** or **thiosulphates** are present, the solution in hydrochloric acid must be heated sufficiently to drive off all the **sulphurous anhydride**, or reactions for oxalates will be obtained, due to the sulphurous acid alone. If there be any doubt as to the complete removal of the sulphurous anhydride, the gas evolved by the reaction of the potassium permanganate should be passed into a solution of calcium hydroxide. A precipitate of calcium carbonate at this point is positive evidence of the previous presence of **oxalic acid or oxalates.**

7. Alkali **ferro-** and **ferricyanides** are separated from each other by the solubility of the latter in alcohol.

8. In testing for nitric acid the student must not be content with good results from **one** test. At least **four** tests should be made, and all of them should give positive results before final affirmative judgment is passed. *Failure* to *bleach indigo solution* in the presence of an *excess of hydrochloric acid* may be taken as conclusive evidence of the *absence of nitrates.*

9. In the analysis of minerals, **silica** or **silicates** will usually be present. The silica should be removed before proceeding with the analysis. Fuse the finely divided material with an excess of sodium carbonate, digest the cooled mass thoroughly in hot water, filter and evaporate the filtrate to dryness. Moisten the residue with concentrated hydrochloric acid, and again evaporate to dryness. Pulverize thoroughly, digest in water acidulated with hydrochloric acid and filter. The residue, white, consists of the silica, SiO_2.

10. **Meta-** or **pyrophosphates** do not react promptly with ammonium molybdate. In the usual course of analysis they are changed to the orthophosphate (§255, 6*A*).

11. **Phosphoric acid** may be detected in the presence of **arsenic acid** by ammonium molybdate if the solution be kept cold; it is preferable to remove the arsenic before testing. In absence of interfering substances the color of the silver nitrate precipitate will indicate the presence or absence of arsenic acid (§69, 6*f*). See also note 26.

12. **Sulphides** which are *transposed by hydrochloric acid* are best detected by the odor of the evolved gas, and by passing the evolved gas into ammonium hydroxide and testing with sodium nitroferricyanide. Other **sulphides** are decomposed by nitric acid or by nitrohydrochloric acid with separation of sulphur as a leathery mass or as a yellow precipitate. Persistent heating of

the sulphur with the reagent decomposing the sulphide will cause the oxidation of a portion of the sulphur to a sulphate which may be detected in the usual manner. A portion of the precipitated sulphur should be burned on a platinum foil with careful observance of the odor of the evolved gas.

13. A **sulphite** (or other lower oxidized compound of sulphur) is readily detected by adding barium chloride in excess to a portion of the solution, dissolving in **HCl**, filtering if residue remains, and adding bromine or chlorine to the clear filtrate. A precipitation of barium sulphate indicates the oxidation of a lower compound of sulphur to a sulphate.

14. It frequently becomes necessary to detect and estimate sulphides, thiosulphates, sulphites and sulphates in mixtures containing two or more of the compounds. The method of procedure will vary according to the nature of the substance. The student will be aided by studying §§**257**, 8; **258**, 8; and **265**, 8.

15. The **recognition** of chlorides, bromides and iodides—by evolving their chlorine, bromine and iodine, *in presence of each other*—can be accomplished as follows—for the iodine the test being very easy; for chlorine, indirect but unmistakable; for bromine, dependent upon much care and discretion.*

The **iodine** is liberated with dilute **chlorine-water**, added drop by drop, and is readily detected by **starch**, **or carbon disulphide**, according to §**280**, 8. (As to interference of thiocyanates, see §**234**.) The **chlorine** is vaporized (from another portion) as *chlorochromic anhydride*, and the latter identified by its color and its various products, as described in §**269**, 8*d*. Before the **bromine** is identified the iodine is to be either *removed as free iodine*, *or oxidized to iodate* (§**276**, 8*b*). The oxidation to iodic acid is effected as follows: Treat with chlorine-water till free iodine no longer shows its color; add a drop or two more of the chlorine-water, and dilute with water, keeping cool; then add the carbon disulphide, agitate and leave the solvent to settle, for the yellow color of bromine. The removal of free iodine may be accomplished as follows: Add chlorine-water, drop by drop, as long as the iodine tint seems to deepen by the addition; add the carbon disulphide, agitate, allow to subside, and remove the lower layer, either by taking it out with a pipette or by filtration through a wet filter. Repeat, if need be, till iodine color is no longer obtained; then continue, with dilute chlorine water, in test for bromine.

Separation by the persulphate method. To ten cc. of the original solution, add slight excess of Na_2CO_3, free from chlorine, and boil, to precipitate the heavy metals. The solution must react alkaline. Filter and add to the filtrate acetic acid, several cc. more than enough to neutralize it, dilute to 50–60 cc., add about one-half gram of $K_2S_2O_8$, and heat. If an iodide is present, free iodine will be liberated, and may be identified by shaking a few drops of the solution with CS_2. Boil in a casserole until all iodine is expelled, which should require three to four minutes. If action is slow, more persulphate should be added. When the solution is colorless, add a few more crystals of persulphate and boil again, to make sure that no iodine remains. As the solution evaporates add distilled water to maintain the original volume. To remove Br' add two cc. of H_2SO_4, previously diluted with water, a little more $K_2S_2O_8$, and heat *to* boiling point, *but do not boil*. A yellow or red coloration, if the separation of **I** has been properly conducted, indicates **Br**. Pour a little of the solution into a test tube, cool, and shake with CS_2, which should be colored yellow or red but not violet, which would indicate that the **I** had not been completely removed. If bromine is present, add one-half gram of $K_2S_2O_8$ to the main part of the solution, and boil until it is all expelled and the solution is colorless; then test with a little more $K_2S_2O_8$ and boil five minutes longer to make sure of the complete expulsion of the bromine. *Be sure that the volume of the solution does not fall below 50 to 60 cc.* Add distilled water from time to time to replace that lost by evaporation. When all bromine is removed,

* In consequence of the relative commercial values of bromine and iodine, and the medicinal relations of bromides and iodides, it is of great importance to search commercial iodides for intentional and considerable mixtures of bromides—an impurity likely to escape cursory chemical examination. There are, however, very *slight* and usually unobjectionable proportions of bromides frequently to be found in the iodides of commerce, and occurring from the difficulty of exact separation in the manufacture of iodine from kelp.

cool and add a few drops of silver nitrate; a white, curdy precipitate of silver chloride indicates the presence of **Cl**. If too much silver nitrate is added, a white crystalline precipitate *may* be formed, but will dissolve upon dilution and warming.

If ClO'_3 is present, the above procedure cannot be followed, for the **I′** would be oxidized in IO'_3. In this case it is necessary to precipitate the **Cl′**, **Br′**, and **I′** by adding to the original solution excess of silver nitrate and then nitric acid; this effects a separation, silver chlorate being soluble. Wash the precipitate of **AgCl**, **AgBr**, **AgI**, transfer to a test tube, add a piece of zinc, a little water, and a drop of sulphuric acid. Let it stand until it is perfectly black all the way through, showing complete reduction to metallic silver. Filter and treat the filtrate containing $ZnCl_2$, $ZnBr_2$, ZnI_2, according to the above method, starting at the beginning. Even if no heavy metals are present, Na_2CO_3 should be added to neutralize any mineral acid that may be present and to form some sodium acetate when acetic acid is added.

The persulphate method should be used only when the presence of **I′** or **Br′** has been proved by some short test (H_2SO_4, **Cl**, HNO_2, HNO_3, or other oxidizer). In presence of a great excess of **Br′**, $CuSO_4$, KNO_2, or **HgCl** is an excellent test for **I′**.

If iodide in large proportion is to be removed, it is well, first, to precipitate it out, as far as possible, by copper sulphate and a reducing agent (*Note 17*). The filtrate is then to be treated by either method above given.

16. The **separation by ammonium hydroxide**, *as a solvent of the silver precipitates*—**AgCl**, **AgBr**, **AgI**—when conducted with dilute ammonium hydroxide, may be made complete between the chloride and the iodide, also between the bromide and the iodide, but it is very imperfect between the bromide and the chloride. The hot and strong solution of ammonium acid carbonate separates the chloride from the bromide (§269, 8*a*).

17. The direct *removal of* **iodides** *by precipitation, leaving bromides and chlorides in solution*, can be effected (approximately) by **copper sulphate with sulphurous acid** (§77, 6*f*), or quite completely by **palladous chloride** (§106, 6).

18. Chloric acid is separated from *hydrochloric and all other acids of chlorine, bromine and iodine* (except from hypochlorous acid, and from traces of bromic acid), by remaining in solution during the precipitation by **silver nitrate** (§273, 5).

19. Chloric acid is separated *from nitric acid*—after finding that *silver nitrate gives no precipitate* in another portion of the solution, acidulated—by evaporating and igniting the residue, then dissolving and testing one portion of the solution by **silver nitrate** for the *chloride* formed from chlorate during ignition (§273, 7). The other portion of the solution is tested for nitric or nitrous acid.

20. If we have to separate chloric acid *both from nitric and hydrochloric acids*, a solution of **silver sulphate** must be used instead of the nitrate, to precipitate out all the hydrochloric acid. The filtrate from this is evaporated, **ignited**, dissolved and tested for silver chloride, indicating chlorate in the original solution, and another portion is tested for nitric acid. Also, chlorates are *distinguished* (not separated) *from nitrates*, by oxidation of **ferrous sulphate** in solution with **acetic acid** on heating, and the consequent formation of the *red solution of ferric acetate* (§§126, 6*b*; 152; 223, 6). The solution tested must contain no free acids, and no nitrites or other oxidizing agents beside the two in question, but may contain chlorides; and, of course, the ferrous sulphate must be pure enough not to color when heated alone with the acetic acid. Mix the ferrous sulphate solution with the acetic acid, boil, then add the solution to be tested, and heat nearly to boiling, for some minutes. If no red color appears, chlorates are absent, and nitrates may be present.

21. **Hypochlorites** are separated *with chlorates* from chlorides (bromides), etc., by **silver nitrate**; and distinguished *from chlorates* (in the filtrate from **AgCl**, etc.) by bleaching litmus, and by their much more rapid decomposition and consequent precipitation of any silver in solution. They are also more active than chlorates, as oxidizing agents.

22. M. Deehan's method (§269, 8*i*) consists (*1*) in boiling the mixture with a solution of 40 grammes of $K_2Cr_2O_7$, dissolved in 100 cc. of water, which lib-

erates and expels all of the iodine without disturbing the bromine and chlorine

$$5K_2Cr_2O_7 + 6KI = Cr_2O_3 + 8K_2CrO_4 + 3I_2$$

(2) 8 cc. of a dilute solution of sulphuric acid (consisting of equal volumes of H_2SO_4 *sp. gr.* 1.84, and water) are added to 100 cc. of the dichromate solution, and on boiling, the bromine is distilled off without disturbing the chlorine; after which the chlorine is detected in the usual manner. For other methods of detecting chlorides in presence of bromides and iodides, see §269, 8.

23. For A. Longi's process for the analysis of a mixture of chlorides, bromides, iodides, chlorates, bromates, iodates, ferrocyanides and ferricyanides, see *C. N.*, 1883, **47**, 209.

24. In the detection of **chlorides** in presence of cyanides and thiocyanates by the decomposition of the silver salts with concentrated sulphuric acid (§269, 8*e*), a drop or two of silver nitrate should be added to the precipitate before heating with the acid or a black precipitate will be obtained, apparently carbon.

25. For the detection of a **bromide** in the presence of an iodide, the most satisfactory method is by the use of potassium chlorate and dilute sulphuric acid as described in §276, 8*c*. The student should carefully note the change in color of the solution. The first very dark color is due to the liberation of iodine. There is usually a sudden change of color on the complete oxidation of the iodine, but if much bromine be present the solution will be quite dark straw color. This should be tested with carbon disulphide and the heating continued if free iodine is still present.

26. **Arsenic acid** should not be present when testing for a phosphate. If the arsenic acid be reduced to arsenous acid by sulphurous acid it will not interfere with the ammonium molybdate test for a phosphate. The excess of sulphurous acid must be removed by boiling before testing for the phosphate. Arsenic is best removed by precipitation as sulphide in the second group.

27. **Chromic acid** is always identified by reduction and precipitation as chromic hydroxide, green, in the third group. The red or yellow color to the original substance usually gives evidence of the probable presence of the hexad chromium. The reduction is effected in the course of analysis by hydrosulphuric acid with precipitation of sulphur. It is advisable to reduce all chromates by warming with hydrochloric acid and alcohol before proceeding with the analysis. Another portion of the substance may be reduced with sulphuric acid and alcohol and tested for chlorides.

28. **Manganates** are readily decomposed by water with formation of $KMnO_4$ and MnO_2. In the presence of a fixed alkali the manganate solution is green and does not rapidly change to permanganate. The **manganates** and **permanganates** in solution are all dark colored (green, purple-red) and should be reduced by warming with hydrochloric acid before proceeding with the analysis.

§319. PRINCIPLES.

In the following statements, the term salt includes only cases where the metal acts as a base, *e. g.*, chromium salts include $CrCl_3$, not K_2CrO_4. Only salts of ordinary metals are included.

1. **Hydroxides** when brought in contact with acids form salts, provided they can be formed by any means in the presence of water. The same is true of oxides. But Al_2S_3 and Cr_2S_3 are not formed in presence of water. (Some oxides after ignition fail to unite with all acids, *e. g.*, SnO_2, Fe_2O_3, Al_2O_3, but by long boiling unite with a few acids; while ignited Cr_2O_3 is insoluble in all acids).

2. All **nitrates, chlorates** and **acetates** are soluble, but salts of cuprosum, bismuth, tin, antimony and the oxysalts of mercury require some free acid to hold them in solution.

3. All **oxides** and **hydroxides** are insoluble, except those of the alkalis, those of **Ba**, **Sr** and **Ca** slightly soluble. The **fixed alkalis** precipitate solutions of all other metallic salts, **Ba**, **Sr** and **Ca** incompletely. The precipitate with silver, antimonosum and mercury is an oxide, with Sn^{IV} it is $SnO(OH)_2$, with Sb^{V}, $SbO(OH)_3$, in all other cases a normal hydroxide. [At boiling heat instead of normal hydroxides other hydroxides are sometimes formed, *e. g.*, $Fe_4O_3(OH)_6$, and $Cu_3O_2(OH)_2$]. This precipitate redissolves in eight cases, forming, if potassium hydroxide be used . . . K_2PbO_2, K_2SnO_2, K_2SnO_3, $KSbO_2$, $KSbO_3$, K_2ZnO_2, $KAlO_2$, $KCrO_2$. The last precipitates on boiling.

4. **Ammonium hydroxide** precipitates solutions of the first four groups, manganese and magnesium imperfectly and not at all if ammonium chloride be present. The precipitate is a normal hydroxide, except that with Sn^{IV} it is $SnO(OH)_2$, with Sb^{V}, $SbO(OH)_3$, with **Ag** and Sb''' the oxide, with **Pb** a basic salt, and with **Hg** a substituted *mercuric* ammonium compound, Hg' in addition forms Hg°. The precipitate redissolves in six cases, viz., silver, copper, cadmium, cobalt, nickel and zinc. Complex ammonium compounds are formed, such as $(NH_3)_2Ag^{+}\ \bar{O}H$ and $(NH_3)_4Zn^{++}\ (OH)_2$.

5. The **chlorides** of the first group are insoluble, lead chloride slightly soluble. **Hydrochloric acid** and **soluble chlorides** precipitate solutions of salts of the first group, lead salts incompletely, and normal lead salts are not precipitated by mercuric chloride. Cuprous chloride is also insoluble. (For action on higher oxides, etc., see §269, 6*A*.)

6. The **bromides** of the first group are insoluble, lead bromide slightly soluble (less than the chloride). **Hydrobromic acid** and **soluble bromides** precipitate solutions of the salts of the first group, lead salts incompletely. (For action on higher oxides, etc., see §276, 6*A*.)

7. The **iodides** of lead, silver, mercury and cuprosum are insoluble. **Hydriodic acid** and **soluble iodides** precipitate solutions of lead, silver, mercury and cuprosum. Cupric salts are precipitated as cuprous iodide with liberation of iodine. Ferric salts are reduced to ferrous, arsenic acid to arsenous acid, Sb^{V} to Sb''' with liberation of iodine.

(Bismuth, stannous and antimonous iodides are really insoluble in water, and are readily formed by the action of hydriodic acid or soluble iodides on the dry or merely moistened salts. But the dissolved salts of these three metals frequently contain so much free acid that it prevents their precipitation by hydriodic acid or by soluble iodides. Arsenous iodide is decomposed by water. It may be formed from the chloride, best by adding hydriodic acid or a soluble iodide to a solution of arsenous acid in strong hydrochloric acid. Bismuth iodide is black; stannous, antimonous and arsenous iodides are yellowish red.)

8. The **sulphates** of lead, mercurosum, barium, strontium and calcium are insoluble, those of calcium and mercurosum slightly soluble. **Sulphuric acid** and **soluble sulphates** precipitate solutions of lead, mercurosum, barium, strontium and calcium; calcium and mercurosum incompletely.

9. (*a*) The **sulphides** of the first four groups are insoluble. **Hydrosulphuric acid** transposes salts of the first two groups in acid, neutral, and alkaline mixtures, except arsenic, which is generally imperfectly precipitated unless some free acid or salt that is not alkaline to litmus paper be present. The result is a sulphide, but mercurosum forms mercuric sulphide and mercury, and arsenic acid forms arsenous sulphide and free sulphur. Ferric solutions are reduced to ferrous with liberation of sulphur. In acid mixture other third and fourth group salts are not disturbed, but from solutions of their normal salts traces of cobalt, nickel, manganese, and zinc are precipitated. (For action on higher oxides, see §**257**, 6*A*).

(*b*) **Soluble sulphides** transpose salts of the first four groups. The result is a sulphide, except that with aluminum and chromium salts it is a hydroxide, hydrosulphuric acid being evolved. With mercurous salts, mercuric sulphide and mercury are formed; with ferric salts, ferrous sulphide and sulphur.

10. The **carbonates** of the **alkalis** are soluble. **Carbonates** of the **fixed alkalis** precipitate solutions of all other metallic salts. The precipitate is:

a. An **oxide** with antimonous salts.

b. A normal **hydroxide** with **Sn″**, **Al**, **Cr‴** and **Fe‴**; with Sn^{IV}, $SnO(OH)_2$; with Sb^{V}, $SbO(OH)_3$.

c. A **normal carbonate** with **Ba**, **Sr** and **Ca** salts and, if cold, with silver, mercurosum, cadmium, ferrosum and manganosum.

d. A **basic carbonate** in other cases, except mercuric chloride, which forms an oxychloride. Carbonic is completely displaced by strong acids, for example, from all carbonates, by **HCl**, $HClO_3$, **HBr**, $HBrO_3$, **HI**, HIO_3, $H_2C_2O_4$, $HC_2H_3O_2$, HNO_3, H_3PO_4, H_2SO_4, and even by H_2S, completely from carbonates of first four groups, incompletely from those of the fifth and sixth groups (Nandin and Montholon, *C. r.*, 1876, **83**, 58).

11. All **normal** and **di-metallic orthophosphates** are insoluble except those of the alkalis. The normal and di-metallic phosphates of the alkalis precipitate solutions of all other salts. The precipitate is a normal, di-metallic, or basic phosphate, except that with mercuric chloride and with the chlorides of antimony it is not a phosphate, but an oxide, or an oxychloride.

All phosphates are dissolved, or transposed by nitric, hydrochloric and sulphuric acids, and all are dissolved by acetic acid except lead, aluminum and ferric phosphates. All are soluble in phosphoric acid except those of lead, tin, mercury and bismuth.

12. **Ignition.**—*a.* The **oxides** of lead and iron heated in the air to a **red heat** form Pb_3O_4 and Fe_2O_3, but at a **white heat** form **PbO** and Fe_3O_4. **Other oxides,** if ignited in the air to a white heat, when changed, either take up or lose oxygen and leave ultimately the following: **Ag, Hg, Au, Pt,** SnO_2, Sb_2O_3, As_2O_3, Bi_2O_3, **CuO, CdO,** Fe_3O_4, Cr_2O_3, Al_2O_3, **CoO, NiO,** Mn_3O_4, **ZnO, BaO, SrO, CaO, MgO,** K_2O, Na_2O. In a few cases ignition at a lower temperature gives other results, *e. g.*, Co_2O_3, BaO_2, Na_2O_2, Sb_2O_4, etc.

b. **Alkali hydroxides** ignited in air at a white heat are not changed. **Other hydroxides** evolve H_2O and leave as in (*a*).

c. **Alkali carbonates** ignited in air at a white heat are not changed. **Other carbonates** evolve CO_2 and leave as in (*a*).

d. **Fixed alkali oxalates** ignited at a white heat in absence of air are changed to carbonates, evolving **CO**. **Ba, Sr** and **Ca** oxalates and a few others at a **red heat,** in **absence** of **air,** form carbonates evolving **CO**, at a **white heat** these carbonates are changed to oxides evolving CO_2. **All oxalates** ignited in **presence** of **air** at a white heat are changed as in (*a*), except the fixed alkali oxalates which are left as carbonates. In all cases when air is present the **CO** burns to CO_2.

e. **All organic** salts ignited at a white heat, in a current of air, leave residues as in (*a*), but forming carbonates if fixed alkalis are present. The products evolved depend upon the composition of the organic portion of the salt.

13. **The following acids** may be made by adding **sulphuric acid** in excess to their respective salts and distilling:

a. Carbonic from all carbonates.

b. Nitric from all nitrates.

d. Sulphurous from all sulphites.

e. Hydrochloric from all chlorides except those of mercury. But sulphuric acid transposes the chlorides of **Ag, Sn** and **Sb** with extreme difficulty, so that practically other methods are used to separate hydrochloric acid from the chlorides of these metals.

§320. Equations.

It is recommended that in the class-room some attention be paid to the balancing of equations as representing the important analytical and synthetic operations, especially those involving oxidation and reduction. The work will be simplified by a careful study of §§216, 217 and 218 and application of the rule as illustrated there. When the time permits, the operations represented by the equations studied in the class-room should be performed by each student at his laboratory work-table. At first the teacher should select simpler equations illustrating analytical operations and the principles (§319). Later, the more difficult equations involving oxidation and reduction should be studied. The student should give the authority for every reaction. The accompanying list of equations is merely suggestive and may be expanded by the teacher as the time permits. In each equation the second substance is to be considered as in excess; that is, sufficient to produce the greatest possible change in the first substance. For description and methods of making the basic salts used in this list, see Dammer's *Anorganishe Chemie.*

1. $Sb + HNO_3$
2. $As_4 + HNO_3$
3. $As_2O_3 + HNO_3$
4. $Mn(OH)_2 + PbO_2 + HNO_3$
5. $MnSO_4 + Pb_3O_4 + H_2SO_4$, dilute
6. $MnO_2 + KNO_3 + K_2CO_3$, fusion
7. $S_2 + KNO_3 + K_2CO_3$, fusion
8. $MnS + KNO_3 + K_2CO_3$, fusion
9. $Mn_3O_{11} + Pb_3O_4 + HNO_3$
10. $Cr(OH)_3 + KNO_3 + K_2CO_3$, fusion.
11. $Pb_3(AsO_4)_2 + Zn + H_2SO_4$, dilute
12. $Cu_2As_2O_7 + Zn + H_2SO_4$, dilute
13. $Pb(NO_3)_2 + Al + KOH$
14. $Cu(NO_3)_2 + Al + KOH$
15. $Bi(NO_3)_3 + Al + KOH$
16. $Hg_{10}O_2(NO_3)_8 + Al + KOH$
17. $MnS + Mn(NO_3)_2 + K_2CO_3$, fus.
18. $Mn_2O_5 + Pb_3O_4 + HNO_3$
19. $Fe + H_2SO_4$, con., hot.
20. $KI + KIO_3 + H_2SO_4$, dilute
21. $MnSO_4 + KMnO_4 + H_2SO_4$, dilute
22. $(NaCl + K_2CrO_4 + H_2SO_4)$, dry, hot
23. $KNO_3 + FeSO_4 + H_2SO_4$, con., cold
24. $K_2Cr_2O(CrO_4)_3 + HCl$, hot
25. $Hg_8O(NO_3)_6 + Al + KOH$
26. $Ag_3AsO_4 + SnCl_2 + HCl$, *sp. gr.* 1.18
27. $PbO_2 + K_2C_2O_4 + H_2SO_4$, dilute
28. Pb_3O_4, white heat
29. NaH_2PO_2, ignition
30. $Fe_6O_9(AsO_3)_2 + FeS + HCl$
31. $FeBr_2 + HNO_3$
32. $Sn + HNO_3$, hot
33. $KOH + Br_2$, hot
34. $FeI_2 + H_2SO_4$, *sp. gr.* 1.84, hot
35. $KBr + KBrO_3 + H_2SO_4$, dilute
36. $FeSO_4 + KMnO_4 + H_2SO_4$, dilute
37. $K_2Cr_2O(CrO_4)_3 + KOH + Br_2$
38. $4Hg_2O_2(N_2O_5)_3 + Al + KOH$
39. $Ag_3AsO_3 + SnCl_2 + HCl$, *sp. gr.* 1.18
40. Co_2O_3, ignition, white heat
41. $H_2S + HNO_3$, *sp. gr.* 1.42, hot
42. $Hg_3(AsO_4)_2 + FeS + HCl$
43. $Fe_8O_9(AsO_3)_2 + KOH + Cl_2$
44. $FeI_2 + HNO_3$, *sp. gr.* 1.48, hot
45. $Cr_2(SO_4)_3 + Cr(NO_3)_3 + K_2CO_3$, fusion
46. $Pb_3(AsO_4)_2 + Zn + H_2SO_4$, dilute
47. $KOH + Cl_2$, cold
48. $KBr + KIO_3 + H_2SO_4$, dilute
49. $(Cr_2OHCl_5 + K_2CrO_4 + H_2SO_4)$, dry, hot
50. $Zn_4O_3(NO_3)_2 + FeSO_4 + H_2SO_4$, concentrated, cold
51. $Hg_3(AsO_4)_2 + SnCl_2 + HCl$, *sp. gr.* 1.18
52. Mn_3O_5, ignition
53. $Fe_2O_2SO_3 + Zn + H_2SO_4$, dilute
54. $Bi_2S_3 + HNO_3$, dilute, hot
55. $Hg_3AsO_4 + FeS + HCl$
56. $Cr_2(OH)_4SO_4 + KOH + Cl_2$
57. $Fe(H_2PO_2)_2 + HNO_3$
58. $Cr_2O_3 + KClO_3 + K_2CO_3$, fusion
59. $Cu_5O_2(AsO_4)_2 + Zn + H_2SO_4$, dil.
60. $KOH + Cl_2$, hot
61. $Mn_3O_{11} + KClO_3 + K_2CO_3$, fusion
62. $HIO_3 + SnCl_2 + HCl$
63. $Bi_{12}O_{13}(NO_3)_{10} + FeSO_4 + H_2SO_4$, con., cold
64. CrO_3, ignition
65. $KMnO_4 + H_2C_2O_4 + H_2SO_4$, dilute
66. $FeAsO_4 + SnCl_2 + HCl$, *sp. gr.* 1.18
67. $Fe_3Cl_8 + FeS + HCl$
68. $5CuO.As_2O_5 + Fe + HCl$
69. $HIO_3 + H_2C_2O_4$, hot
70. $(Cr_2(OH)_5Cl + K_2Cr_2O_7 + H_2SO_4)$, dry, hot
71. $Fe(NO_3)_2 + FeSO_4 + H_2SO_4$, con., cold
72. $Ag_2SO_4 + Zn$
73. $H_2SO_3 + HNO_3$, *sp. gr.* 1.42
74. $FeAsO_4 + FeS + HCl$
75. $Pb(AsO_2)_2 + KOH + Cl_2$
76. $Fe(NO_3)_2 + HNO_3$
77. $Mn_3O_5 + Mn(NO_3)_2 + K_2CO_3$, fusion
78. $Fe_6O_9(AsO_3)_2 + KOH + Br_2$
79. $Pb_{10}O_8(OH)_8(NO_3)_6 + Al + KOH$

§321. Problems in Synthesis.

For the sake of a more thorough drill in the principles of oxidation and other reactions, a few problems are here given; a part of them the student should practically work at his table, but they are chiefly designed for class exercises. Special care should be taken that a pure product be formed and that the ingredients be taken from the sources indicated. In each case the authority for every step in the process should be stated.

1. Silver oxide from metallic silver.
2. Mercuric bromide from mercurous chloride and sodium bromide.
3. Chromic chloride from potassium chromate and hydrochloric acid.
4. Arsenic acid from potassium arsenite.
5. Potassium arsenate from arsenous oxide and potassium hydroxide.
6. Lead nitrate from lead chloride and potassium nitrate.
7. Mercurous nitrate from mercuric chloride and sodium nitrate.
8. Mercurous oxide from mercuric oxide.
9. Mercuric bromide from metallic mercury and potassium bromide.
10. Lead nitrate from lead dioxide and potassium nitrate.
11. Lead chromate from lead hydroxide and chromium hydroxide.
12. Barium chromate from chrome alum and barium carbonate.
13. Mercuric chromate from mercuric sulphide and chromium hydroxide.
14. Chromium sulphate from potassium dichromate and zinc sulphide.
15. Phosphoric acid from sodium phosphate.
16. Phosphorus from calcium phosphate.
17. Lead iodate from sodium iodide and lead sulphide.
18. Silver iodate from silver chloride and iodine.
19. Ferric arsenate from ferrous sulphide and arsenous oxide.
20. Mercuric bromide from mercuric sulphide and sodium bromide.
21. Ammonium sulphate from ammonium chloride and sulphur.
22. Sodium chloride from commercial salt.
23. Phosphorus from sodium phosphate.
24. Lead sulphide from trilead tetroxide and ferrous sulphide.
25. Ferrous sulphate from ferric oxide and sulphuric acid.
26. Ammonium hydroxide from potassium nitrate.
27. Cadmium sulphate from cadmium phosphate and ferrous sulphide.
28. Mercurous nitrate from mercuric sulphide and nitric acid.
29. Barium sulphate from potassium thiocyanate and barium chloride.
30. Mercurous chloride from mercuric oxide and sodium chloride.
31. Sodium iodate from potassium iodate and sodium chloride.
32. Sodium phosphate from calcium phosphate and sodium chloride.
33. Strontium nitrate from sodium nitrate and strontium sulphate.
34. Potassium sulphate from potassium nitrate and sulphur.
35. Barium sulphate from barium chloride and zinc sulphide.
36. Potassium permanganate from manganese dioxide and potassium nitrate.
37. Arsenous chloride from lead arsenate and sodium chloride.
38. Potassium chromate from potassium nitrate and lead chromate.
39. Potassium iodide from potassium chloride and iodine.
40. Barium chlorate from sodium chloride and barium nitrate.
41. Arsenous sulphide from arsine and ferrous sulphide.
42. Copper sulphate from copper sulphide.
43. Silver nitrite from silver chloride and sodium nitrate.
44. Cuprous chloride from metallic copper and sodium chloride.
45. Manganous carbonate from manganese peroxide and sodium carbonate.
46. Manganous pyrophosphate from manganese peroxide and ammonium phosphate.
47. Lead arsenate from lead sulphide and arsenous oxide.
48. Bismuth subnitrate from metallic bismuth and nitric acid.
49. Barium perchlorate from sodium chloride and barium hydroxide.
50. Lead iodate from metallic lead and iodine.

§322. Table of Solubilities.*

Showing the classes to which the compounds of the commonly occurring elements belong in respect to their solubility in water, hydrochloric acid, nitric acid, or aqua regia.

Preliminary Remarks.

For the sake of brevity, the classes to which the compounds belong are expressed in letters. These have the following signification:

W or w, soluble in water.

A or a, insoluble in water, but soluble in hydrochloric acid, nitric acid, or in aqua regia.

I or i, insoluble in water, hydrochloric acid, or nitric acid.

Further, substances standing on the border-lines are indicated as follows:

W—A or w—a, difficultly soluble in water, but soluble in hydrochloric acid or nitric acid.

W—I or w—i, difficultly soluble in water, the solubility not being greatly increased by the addition of acids.

A—I or a—i, insoluble in water, difficultly soluble in acids.

If the behavior of a compound to hydrochloric and nitric acids is essentially different, this is stated in the notes.

Capital letters indicate common substances used in the arts and in medicine, while the small letters are used for those less commonly occurring.

The salts are generally considered as normal, but basic and acid salts, as well as double salts, in case they are important in medicine or in the arts, are referred to in the notes.

The small numbers in the table refer to the following notes.

Notes to Table of Solubilities.

(1) Potassium dichromate, W. (2) Potassium borotartrate, W. (3) Hydrogen potassium oxalate, W. (4) Hydrogen potassium carbonate, W. (5) Hydrogen potassium tartrate, W. (6) Ammonium potassium tartrate, W. (7) Sodium potassium tartrate, W. (8) Ammonium sodium phosphate, W. (9) Acid sodium borate W. (10) Hydrogen sodium carbonate, W. (11) Tricalcium phosphate, A. (12) Ammonium magnesium phosphate, A. (13) Potassium aluminum sulphate, W. (14) Ammonium aluminum sulphate, W. (15) Potassium chromium sulphate, W. (16) Zinc sulphide, as sphalerite, soluble in nitric acid with separation of sulphur; in hydrochloric acid, only upon heating. (17) Manganese dioxide, easily soluble in hydrochloric acid; insoluble in nitric acid. (18) Nickel sulphide is rather easily decomposed by nitric acid; very difficulty by hydrochloric acid. (19) Cobalt sulphide, like nickel sulphide. (20) Ammonium ferrous sulphate, W. (21) Ammonium ferric chloride, W.

* The following table of solubilities, is taken from Fresenius Qualitative Analysis, Well's translation of 16th German edition.

SOLUBILITY

	Potassium.	Sodium.	Ammonium.	Barium.	Strontium.	Calcium.	Magnesium.	Aluminum.	Chromium.	Zinc.	Manganese.	Nickel.	Cobalt.
Oxide.....	W	W	W	W	w	W-A	A	A	A & I	A	a_{17}	A	A
Chromate.	W_1	w	w	a	w-a	w-a	w		a	w	w	a	a
Sulphate..	$W_{13\cdot15}$	W	$W_{14\cdot26\cdot30}$	I	I	W-I	W	$W_{13\cdot14}$	W & I_{15}	W	W	W	W
Phosphate	w	W_8	$w_{8\cdot12}$	a	a	A_{11}	a_{12}	a	a	a	a	a	a
Borate	w_2	w_9	w	a	a	a	w-a	a	a	a	a	a	a
Oxalate...	W_3	W	W	a	a	A	a	a	w-a	a	w-a	a	a
Fluoride..	w	w	W	w-a	w-a	A-I	a-i	w	w	w-a	a	w-a	w-a
Carbonate	W_4	W_{10}	W	A	A	A	A			A	A	A	A
Silicate...	W	W		a	a	a	a	a-i	a	a	a	a	a
Chloride..	W_{27}	W_{36}	$W_{21\cdot38}$	W	W	W	W	w	W & I	W	W	W	W
Bromide..	W	W	w	w	w	w	w	w	w & i	w	w	w	w
Iodide.....	W	w	W	w	w	w	w	w	w	w	w	w	w
Cyanide...	W	w	w	w-a	w	w	w		a	A	a	a-i	a-i
Ferrocy'de	W	w	w	w-a	w	w	w			A-I	a	i	i
Ferricy'de	W	w	w			w	w			a	i	i	i
S'lphocy'de	W	w	W	w	w	w	w		w	w	w	w	w
Sulphide..	W	W	W	W	w	W-A_{45}	a	a	a-i	A_{16}	A	a_{18}	a_{19}
Nitrate...	W	W	W	W	W	w	w	w	W	w	w	w	W
Chlorate..	W	w	w	w	W	w	w	w	w	w	w	w	w
Tartrate..	$W_{5\cdot6\cdot7\cdot22\cdot46}$	W_7	w_6	a	a	A	w-a	w	w	a	w-a	a	w
Citrate....	w	w	w	a	a	w-a	w	w	w	w a	a	w	w
Malate	w	w	w	w & a	w	w-a_{47}	w	w		w	w		
Succinate.	w	w	w	w-a	w-a	w-a	w	w-a		w-a	w	w	w-a
Benzoate..	w	w	w	w		w	w				w		
Salicylate.	w	W	W	w-a	w-a	w-a	w						
Acetate...	W	W	W	W	w	W	w	W	w	W	w	w	w
Formate..	w	w	w	w	w	w	w	w	w	w	w	w	w
Arsenite..	W	w	w	a	a	a	a				a	a	a
Arsenate..	W	W	w	a	a	a	a	a	a	a	a	a	a

TABLE.

Ferrous.	Ferric.	Silver.	Lead.	Mercurous.	Mercuric.	Cupric.	Bismuth.	Cadmium.	Gold.	Platinum.	Stannous.	Stannic.	Antimonous.	
a	A	a	A_{24}	A	A	A	a	a		a	a	a & i	A_{43}	Oxide
	w	a	A–I	a	w-a	w	a	a			a		a	Chromate
W_{20}	W	W–A	A–I	w-a	W_{27}	W_{30}	w	W		w	w		a	Sulphate
a	A	a	a	a	a	a	a	a			a	a	w-a	Phosphate
a	a	a	a			a	a	w-a			a			Borate
a	a	a	a	a	a	a	a	a		w	a	w	a	Oxalate
w-a	w	w	a		w-a	a	w	w-a			w	w	w	Fluoride
A		a	A	a	a	A	a	a						Carbonate
a	a		a			a		a						Silicate
W	W_{21}	I	W–I	A–I	W_{28}	W	W–A_{33}	W	W_{35}	$W_{37\cdot38}$	W	W_{40}	W–A_{42}	Chloride
w	w	i	w–i	a–i	w	w	w-a	W	w	w			w-a	Bromide
W	w	i	W–A	A	A	w	a	W	a	i	w	w	w-a	Iodide
a–i		I	a		W	a		a	W	w				Cyanide
i	I	i	a			i					i	i		Ferrocy'de
I	w	i	w-a								i			Ferricy'de
w	w	i	a	A	w	a		w-a		a		w		Sulphocy'de
A	a	a_{23}	A	A	A_{29}	a_{31}	a	A	a_{36}	a_{39}	a_{41}	a_{41}	$A_{44\cdot45}$	Sulphide
w	w	W	W	W_{26}	W	W	W_{34}	w		w				Nitrate
w	w	w	w	w	w	w	w	w			w			Chlorate
w-a	$W_{2\cdot}$	a	a	w-a	a	w	a	w-a			a		a_{46}	Tartrate
w	W	a	a	a	w-a	w		a						Citrate
	W	w-a	w-a	a	w-a	w					w	w		Malate
w-a	a	a	a	a	w-a	w		w				a		Succinate
w	a	w-a	a	a	w-a	a		w						Benzoate
		w-a	w-a			w								Salicylate
w	W	w	W_{25}	w-a	w	W_{32}	w	w			w	w		Acetate
w	W	w	w-a	w	w	w	w	w			w			Formate
a	a	a	a	a	a	A							a	Arsenite
a	a	a	a	a	a	a	a					a	a	Arsenate

(22) Potassium ferric tartrate, W. (23) Silver sulphide, only soluble in nitric acid. (24) Minium is converted by hydrochloric acid into lead chloride; by nitric acid, into soluble lead nitrate and brown lead peroxide which is insoluble in nitric acid. (25) Tribasic lead acetate, W. (26) Mercurius solubilis Hahnemanni, A. (27) Basic mercuric sulphate, A. (28) Mercuric chloride-amide, A. (29) Mercuric sulphide, not soluble in hydrochloric acid, nor in nitric acid, but soluble in aqua regia upon heating. (30) Ammonium cupric sulphate, W. (31) Copper sulphide is decomposed with difficulty by hydrochloric acid, but easily by nitric acid. (32) Basic cupric acetate, partially soluble in water, and completely in acids. (33) Basic bismuth chloride, A. (34) Basic bismuth nitrate, A. (35) Sodium auric chloride, W. (36) Gold sulphide is not dissolved by hydrochloric acid, nor by nitric acid, but it is dissolved by hot aqua regia. (37) Potassium plantinic chloride, W—I. (38) Ammonium platinic chloride, W—I. (39) Platinum sulphide is not attacked by hydrochloric acid, is but slightly attacked by boiling nitric acid (if it has been precipitated hot), but is dissolved by hot aqua regia. (40) Ammonium stannic chloride, W. (41) Stannous sulphide and stannic sulphide are decomposed and dissolved by hot hydrochloric acid, and are converted by nitric acid into oxide which is insoluble in an excess of nitric acid. Sublimed stannic sulphide is dissolved only by hot aqua regia. (42) Antimonous oxide, soluble in hydrochloric acid, not in nitric acid. (43) Basic antimonous chloride, A. (44) Antimony sulphide is completely dissolved by hydrochloric acid, especially upon heating; it is decomposed by nitric acid, but dissolved only to a slight degree. (45) Calcium antimony sulphide, W—A. (46) Potassium antimony tartrate, W. (47) Hydrogen calcium malate, W.

§323. Reagents.*

During the past two years the reagents for use in qualitative chemical analysis at the University of Michigan have been made up on the basis of the normal solution; *i. e.*, the quantity capable of combining with one gram of hydrogen or with its equivalent is taken in a litre for the normal solution. For example: Normal potassium hydroxide, **KOH**, requires 56.1 grams per litre of solution (not 56.1 grams to a litre of water), but the usual pure product contains about ten per cent of moisture, so it is directed to use 62.3 grams or 312 grams for a solution five times the normal strength, 5N. Barium chloride, $BaCl_2.2H_2O$, has a molecular weight of 244.2, but the hydrogen equivalent is (244.2 ÷ 2) 122.1, so for a litre of half-normal solution, N/2, take 61 grams.

In the following list of reagents, in the parenthesis immediately following the formula are given the grams per litre necessary for a solution of the strength indicated. Fresenius' standard follows the parenthesis.

Acid, Acetic, $HC_2H_3O_2$ (300, 5N), *sp. gr.* 1.04, 30 per cent acid.
Arsenic, $H_3AsO_4.\frac{1}{2}H_2O$ (15, ½ H_3AsO_4 ÷ 5).
Fluosilicic, H_2SiF_6, §247.
Hydrobromic, HBr (40, N/2).
Hydriodic, HI (64, N/2).
Hydrochloric, HCl (182, 5N, *sp. gr.* 1.084), *sp. gr.* 1.12, 24 p. c. acid.
Hydrosulphuric, H_2S, saturated aqueous solution, §257, 4.
Iodic, HIO_3 (15, ½, HIO_3 ÷ 6).
Nitric, HNO_3 (315, 5N, *sp. gr.* 1.165), *sp. gr.* 1.2, 32 p. c. acid.
Nitrohydrochloric, about one part of concentrated HNO_3 to three parts HCl.
Nitrophenic, $C_6H_2(NO_2)_3OH$ (picric acid).
Oxalic, $H_2C_2O_4.2H_2O$, crystals dissolved in 10 parts water.
Phosphoric, H_3PO_4 (16, N/2).
Sulphuric, H_2SO_4, concentrated, *sp. gr.* 1.84.
Sulphuric, dilute (245, 5N, *sp. gr.* 1.153), one part acid to five parts water.
Sulphurous, H_2SO_3, saturated aqueous solution.
Tartaric, $H_2C_2H_4O_6$, crystals dissolved in three parts water.
Alcohol, C_2H_6O, *sp. gr.* 0.815, about 95 p. c.
Aluminum Chloride, $AlCl_3$ (22, N/2).
Nitrate, $Al(NO_3)_3.7\frac{1}{2}H_2O$ (58, N/2).
Sulphate, $Al_2(SO_4)_3.18H_2O$ (55, N/2).
Ammonium Carbonate, $(NH_4)_2CO_3$ (240, 5N), one part crystallized salt in four parts water, with one part ammonium hydroxide.
Ammonium Chloride, NH_4Cl (267, 5N), one part salt in eight parts water.
Hydroxide, NH_4OH ($85NH_3$, 5N, *sp. gr.* 0.964), *sp. gr.* 0.96, 10 p. c. NH_3.
Ammonium Molybdate, $(NH_4)_2MoO_4$ ($36MoO_3$, N/2, §75, 6*d*), 150 g. salt in one litre of NH_4OH, pour this into one litre of HNO_3, *sp. gr.* 1.2.
Ammonium Oxalate, $(NH_4)_2C_2O_4.H_2O$ (40, N/2), one part crystallized salt in 24 parts water.
Ammonium Sulphate, $(NH_4)_2SO_4$ (33, N/2).
Sulphide, $(NH_4)_2S$, colorless, three parts NH_4OH, saturate with H_2S and add two parts of NH_4OH.

*In the greater number of cases, reagents should be "chemically pure." Different uses require different degrees of purity. An article of sodium hydroxide contaminated with chloride may be used in some operations; not in others. Those who have had training in analysis can do without specific directions, which cannot be made to cover all circumstances; and the beginner must depend on others for the selection of reagents.

Ammonium Sulphide, $(NH_4)_2S_X$, yellow, allow the colorless to stand for some time or add sulphur.
Antimonic Chloride, $SbCl_5$ (30, N/2).
Antimonous Chloride, $SbCl_3$ (38, N/2).
Arsenous Oxide, As_2O_3 (8, N/4), saturated aqueous solution.
Barium Carbonate, $BaCO_3$, freshly precipitated.
Chloride, $BaCl_2.2H_2O$ (61, N/2), one part salt to 10 parts water.
Hydroxide, $Ba(OH)_2.8H_2O$ (32, N/5), saturated aqueous solution.
Nitrate, $Ba(NO_3)_2$ (65, N/2), one part to 15 of water.
Bismuth Chloride, $BiCl_3$ (52, N/2, use **HCl**).
Nitrate, $Bi(NO_3)_3.5H_2O$ (40, N/4, use HNO_3).
Cadmium Chloride, $CdCl_2$ (46, N/2).
Nitrate, $Cd(NO_3)_2.4H_2O$ (77, N/2).
Sulphate, $CdSO_4.4H_2O$ (70, N/2).
Calcium Chloride, $CaCl_2.6H_2O$ (55, N/2), dissolve in 5 parts water.
Hydroxide, $Ca(OH)_2$, a saturated solution in water.
Nitrate, $Ca(NO_3)_2.4H_2O$ (59, N/2).
Sulphate, $CaSO_4.2H_2O$, a saturated solution in water.
Carbon Disulphide, CS_2, colorless.
Chromic Chloride, $CrCl_3$ (26, N/2).
Nitrate, $Cr(NO_3)_3$ (40, N/2).
Sulphate, $Cr_2(SO_4)_3.18H_2O$ (60, N/2).
Cobaltous Nitrate, $Co(NO_3)_2.6H_2O$ (73, N/2), in 8 parts of water.
Sulphate, $CoSO_4.7H_2O$ (70, N/2).
Copper Chloride, $CuCl_2.2H_2O$ (43, N/2).
Nitrate, $Cu(NO_3)_2.6H_2O$ (74, N/2).
Sulphate, $CuSO_4.5H_2O$ (62, N/2), in 10 parts water.
Cuprous Chloride, CuCl (50, N/2, use **HCl**).
Ferric Chloride, $FeCl_3$ (27, N/2), 20 parts water to one part metal.
Nitrate, $Fe(NO_3)_3.9H_2O$ (67, N/2).
Ferrous Sulphate, $FeSO_4.7H_2O$ (80, N/2), use a few drops of H_2SO_4.
Gold Chloride, $HAuCl_4.3H_2O$, solution in 10 parts water.
Hydrogen Peroxide, 3 p. c. solution.
Indigo Solution, 6 parts fuming H_2SO_4 to one part indigo, pulverize, stir and cool, allow to stand 48 hours and pour into 20 parts water.
Lead Acetate, $Pb(C_2H_3O_2)_2.3H_2O$ (95, N/2), dissolve in 10 parts of water.
Chloride, $PbCl_2$, saturated solution, N/7.
Nitrate, $Pb(NO_3)_2$ (83, N/2).
Magnesia Mixture: $MgSO_4$, 100 g.; NH_4Cl, 200 g.; NH_4OH, 400 cc.; H_2O, 800 cc. One cc. = 0.01 g. P.
Magnesium Chloride, $MgCl_2.6H_2O$ (51, N/2).
Nitrate, $Mg(NO_3)_2.6H_2O$ (64, N/2).
Sulphate, $MgSO_4.7H_2O$ (62, N/2), in 10 parts of water.
Manganous Chloride, $MnCl_2.4H_2O$ (50, N/2).
Nitrate, $Mn(NO_3)_2.6H_2O$ (72, N/2).
Sulphate, $MnSO_4.7H_2O$ (69, N/2).
Mercuric Chloride, $HgCl_2$ (68, N/2), in 16 parts of water.
Nitrate, $Hg(NO_3)_2$ (81, N/2).
Sulphate, $HgSO_4$ (74, N/2).
Mercurous Nitrate, $HgNO_3$ (131, N/2), one part salt, 20 parts water and one part HNO_3.
Nickel Chloride, $NiCl_2.6H_2O$ (59, N/2).
Nitrate, $Ni(NO_3)_2.6H_2O$ (73, N/2).
Sulphate, $NiSO_4.6H_2O$ (66, N/2).
Palladous Sodium Chloride, Na_2PdCl_4, in 12 parts water.
Potassium Arsenate, K_3AsO_4 (26, $\frac{1}{2}$ $K_3AsO_4 \div 5$).
Arsenite, $KAsO_2$ (24, $\frac{1}{2}$ $KAsO_2 \div 3$).
Bromate, $KBrO_3$ (14, $\frac{1}{2}$ $KBrO_3 \div 6$).
Bromide, KBr (60, N/2).
Carbonate, K_2CO_3 (207, 3N).
Chlorate, $KClO_3$, the dry salt.
Chloride, KCl (37, N/2).

Potassium Chromate, K_2CrO_4 (49, N/2), in 10 parts water.
Cyanide, **KCN** (33, N/2), in four parts water.
Dichromate, $K_2Cr_2O_7$ (38, ½, $K_2Cr_2O_7 \div 4$), in 10 parts water.
Ferrocyanide, $K_4Fe(CN)_6.3H_2O$ (53, N/2), 12 parts water.
Ferricyanide, $K_3Fe(CN)_6$ (55, N/2), in 10 parts water.
Hydroxide, **KOH** (312 [90 p. c. **KOH**], 5N).
Iodate, KIO_3 (18, ½ $KIO_3 \div 6$).
Iodide, **KI** (83, N/2), dissolve in 20 parts water.
Mercuric Iodide, K_2HgI_4, Nessler's solution, §**207**, 6*k*.
Nitrate, KNO_3 (50, N/2), the crystallized salt.
Nitrite, KNO_2, the dry salt.
Pyroantimonate, $K_2H_2Sb_2O_7.6H_2O$, see §**70**, 4*c*.
Permanganate, $KMnO_4$ (16, ½ $KMnO_4 \div 5$).
Thiocyanate, **KCNS** (49, N/2), in 10 parts water.
Hydrogen Sulphate, $KHSO_4$, fused salt.
Sulphate, K_2SO_4 (44, N/2), in 12 parts of water.
Platinic Chloride, $H_2PtCl_6.6H_2O$, in 10 parts of water.
Silver Nitrate, $AgNO_3$ (43, N/4), in 20 parts of water.
Sulphate, Ag_2SO_4, saturated solution, N/13.
Sodium Acetate, $NaC_2H_3O_2.3H_2O$, in 10 parts of water.
Carbonate, Na_2CO_3 (159, 3N), one part anhydrous salt or 2.7 parts of the crystals, $Na_2CO_3.10H_2O$, in 5 parts of water.
Chloride, **NaCl** (29, N/2).
Tetraborate, $Na_2B_4O_7.10H_2O$, *borax*, the crystallized salt.
Hydroxide, **NaOH** (220 [90 p. c. **NaOH**], 5N), dissolve in 7 parts of water.
Hypochlorite NaClO, §**270**, 4.
Nitrate, $NaNO_3$ (43, N/2).
Phosphate, $Na_2HPO_4.12H_2O$ (60, N/2), dissolve in 10 parts of water.
Phosphomolybdate, §**75**, 6*d*.
Sulphate, (35, N/2).
Sulphide, Na_2S, one part **NaOH** saturated with H_2S to one part of **NaOH**, unchanged.
Acid Sulphite, the dry salt.
Sulphite, $Na_2SO_3.7H_2O$ (63, N/2), in 5 parts of water.
Acid Tartrate, $NaHC_4H_4O_6$, in 10 parts of water
Thiosulphate, $Na_2S_2O_3.5H_2O$, in 40 parts of water.
Stannic Chloride, $SnCl_4$ (33, N/2).
Stannous Chloride, $SnCl_2.2H_2O$ (56, N/2), in 5 parts water strongly acid with **HCl**.
Strontium Chloride, $SrCl_2.6H_2O$ (67, N/2).
Nitrate, $Sr(NO_3)_2$ (53, N/2).
Sulphate, $SrSO_4$, a saturated aqueous solution.
Zinc Chloride, $ZnCl_2$ (34, N/2).
Nitrate, $Zn(NO_3)_2.6H_2O$ (74, N/2).
Sulphate, $ZnSO_4.7H_2O$ (72, N/2).

INDEX.

PAGE

Acetates, detection of..... 258
ignition of..... 267
with ferric salts..... 157
Acetic acid.....256–258
estimation of..... 258
formation of..... 257
glacial..... 257
occurrence of..... 257
preparation of..... 257
properties of..... 256
reactions of..... 257
solubilities of..... 257
Acids, detection of, notes on..... 401
displacement of weak by strong... 185
effect of concentrated sulphuric upon..... 390
list of..... 13
precipitated by barium and calcium chlorides..... 398
preparation of..... 408
separation from bases..... 381
table of, precipitated by silver nitrate..... 399
table of separation of..... 400
Alabandite..... 177
Alabaster..... 216
Alkali carbonates, with third and fourth group salts..... 143
group..... 227
hydroxides, action on double cyanides..... 272
hydroxides, detection of in presence of carbonates..... 270
hydroxides, reactions with..... 227
Alkalis, on third and fourth group metals..... 141
Alkali metals..... 5
Alkaline earth metals..... 5
earth metals in presence of phosphates..... 226
earths, relative solubilities of..... 210
Alkali sulphides, as reagents....317, 318
action of, on stannic salts..... 86
action of, on stannous salts..... 85
Alloys, analysis of..... 379
with copper..... 104

PAGE

Alluvial sand..... 91
Alpha iron..... 154
Aluminum.....144–148
acetate..... 146
compounds, ignition of..... 147
detection of.....147, 166
distinction from chromium..... 150
estimation of..... 147
hydroxide, formation and properties..... 145
hydroxide, solubility in ammonium chloride..... 164
occurrence of..... 144
oxidation of..... 148
oxide and hydroxides..... 145
phosphate, separation of.....146, 147
preparation of..... 144
properties of..... 144
reduction of.....147, 148
salts, reactions of..... 145
salts, with hydrosulphuric acid.... 146
salts, with phenylhydrazin..... 146
separation of, from **Cr** and 4th group by basic acetates..... 145
separation of, from iron by $Na_2S_2O_3$ and Na_2SO_3..... 146
separation of, from glucinum..... 201
solubilities..... 144
Alums..... 147
Ammonia, occurrence..... 235
formation of, from nitric acid..... 286
preparation of..... 235
properties of..... 235
Ammonium.....235–239
arsenomolybdate.....62, 98
benzoate, in separation of **Cu** from **Cd**..... 107
carbonate, as a reagent..... 236
carbonate, in separation of **As, Sb** and **Sn**..... 120
chloride, as a reagent..... 237
chloride, in the third group..... 164
chloride, with $PtCl_4$..... 95
compounds, solubilities of..... 235
cyanate in formation of urea..... 279
detection of..... 238

PAGE

Ammonium, directions for detection 242
estimation of 238
hydroxide, as a reagent 236
hydroxide, as a distinguishing reagent for the first group 53
hydroxide, detection by mercuric chloride 238
hydroxide, preparation and properties of 235
molybdate, preparation of 98
molybdate, test for phosphates 311
molybdate, with arsenic acid 67
oxidation of 239
phosphomolybdate 98
picrate, formation of 236
polysulphide, formation of 237
salts, detection by Nessler's reagent 237
salts, ignition of 238
solution to be tested for 242
sulphate, in separation of strontium and calcium 226
sulphide, as a reagent 237
sulphide, formation of 236
sulphide, preparation of 316
sulphide, on iron and zinc groups 191
sulphide, yellow, formation of 115
sulphide, yellow, in separation of cobalt and nickel 190
sulphide, yellow, in cupric salts 118
test for nitric acid 288–289
thioacetate as a substitute for hydrosulphuric acid 316
Analysis of alkali group 242
proximate 14
operations of 13, 20
ultimate 14
Anatase 205
Anglesite 29
Anions, table of separations of 400
Antimonic acid 76
distinction from antimonous 123
reduction to antimonous by stannous chloride 78
salts, action of hydriodic acid on 78
sulphide, precipitation of 77
Antimonites 74
Antimonous argentide 79
compounds with silver nitrate 78
iodide, formation of 78
oxide, formation of 76
salts with permanganates 78
salts with chromates 78

PAGE

Antimonous sulphide 74
sulphide, precipitation of 77
Antimony 72–82
acids of 72
compounds, reduction with charcoal 80
detection of, in alloys 379
detection of 80
detection of traces of 123
distinction from arsenic 78
estimation of 81
in the test for aluminum 166–167
metal with hydrosulphuric acid 66
mirror 65
notes on analysis of 123
occurrence of 72
oxidation of 81
oxides of 72
pentachloride 74
preparation of 72
properties of 72
reduction of 81
reduction to metallic 79
salts 74
separation from arsenic by peroxide of hydrogen 121
separation from arsenic 65
separation from tin by sodium thiosulphate 78
separation from tin 81
solubility of 73
spots 66
sulphide, separation from arsenous sulphide 123
sulphide, separation from stannous sulphide 123
with iodine 66
Apatite 216, 297
Aragonite 216
Argentite 46
Argol, purification of 260
Argyrodite 137
Arrhenius 20
Arsenates, distinction from arsenites 70, 71
separation from phosphates 402
Arsenic 56–72
acid, precipitation by hydrosulphuric acid 114
acid, reduction by hydrosulphuric acid and hydriodic acid 61
acid, reduction with sulphurous acid 60
acid, with ammonium molybdate 67
acid, with molybdates 62

PAGE

Arsenic acid, with nitric acid 66
acid with silver nitrate 67
antidote for 62
compounds, ignition of 69
compounds, with concentrated hydrochloric acid 61
compounds, with magnesium salts 61
compounds, with stannous chloride 89
detection of 70
detection of, in poisoning 68
distinction from antimony 78
estimation of 70
in glass tubing 70
metal with hydrosulphuric acid ... 66
method of Fresenius and Babo 68
mirror 64, 65
notes on analysis of 122
oxidation of 71
oxides of 57
occurrence of 57
pentasulphide, formation and properties of 60
preparation of 57
properties of 56
reaction with alkali sulphides 59
reaction with hydrosulphuric acid 59
reduction of 71
reduction by stannous chloride 61
separation from antimony 65
separation from antimony by peroxide of hydrogen 121
separation from **Sb** and **Sn** by use of thiosulphates 60
spots, formation of 64
spots, properties of 66
sulphide, separation of, from Sb_2S_3 123
sulphides with ammonium carbonate 120
trichloride, formation in analysis 61
with peroxide of hydrogen 71
with hydrosulphuric acid gas 67
with iodine 66
with nitric acid 66
Arsenites, distinction from arsenates 123
Arsenopyrite 57
Arsenous hydride 64
oxide, crystals, identification of ... 67
sulphide, solubilities of 58
sulphide, with **HCl** gas 67
Arsine 64
from alkaline mixtures 64

PAGE

Arsine reactions with **KOH** 123
separation from stibine 65
with hydrosulphuric acid 60, 65
Asbestos 299
Asbolite 167
Atomic weights, table of 1
Avogadro's Hypothesis 21
Azoimide (hydronitric acid) 282
Azomide 8, 282

Barite 211
Barium 211–214
carbonate, action on ferric salts. 156–157
carbonate, as a reagent 212
carbonate, as a reagent for third and fourth groups 143
carbonate, as a reagent to precipitate chromium 150
carbonate, and ferric salts 156–7
carbonate, to separate phosphates from third, fourth and fifth groups 194
chloride, separation of, from $SrCl_2$ and $CaCl_2$ by **HCl** 212
detection of 214
estimation of 214
hydroxide, formation of 211
iodide, properties 370
occurrence of 211
oxide, preparation of 211
peroxide, ignition of 296
peroxide, preparation 211
preparation of 211
properties of 211
salts, separation of sulphites from sulphates 213
salts, spectrum of 213
separation of, from **Sr**, **Ca** and **Mg** by sulphates 213
solubilities of 212
strontium and calcium, separation of by alcohol 226
sulphate, separation 215
Bases, alkali 12
alkaline earth 12
copper, group of 11
definition of 3
fifth group of 12
first group of 11
fourth group of 12
iron group of 12
need for separation from acids. 380, 381
second group of 11
silver group of 11
sixth group of 12

PAGE

Bases, third group of 12
tin group of 11
zinc group of 12
Bauxite 144
Beryl 200
Beryllium 200
Beta iron 154
Bismite 100
Bismuth 100–104
blowpipe, reactions of 103
chloride, sublimation of 103
detection as iodide 103
detection by alkaline stannite 103
detection by cinchonine 102
detection in alloys 379
detection of 103
detection of traces of 102
dichromate 103
estimation of 103
hydroxide, solubility in glycerol ... 101
iodide, stability toward water 103
nitrate, precipitation with **HCl** 101
nitrate, reactions 101
notes on analysis of 130
occurrence of 100
oxidation of 104
oxides and hydroxides of 100
oxychloride, formation of 101
pentoxide, reaction with halogen acids 101
preparation of 100
properties of 100
reactions of, comparisons with **Cu** and **Cd** 112
reduction by grape sugar 104
salts, reaction with the alkalis 101
separation from **Cu** by glycerol ... 101
solubility of 100
sulphide, formation of 102
sulphide, separation of, from **CuS** 102
sulphide, separation of, from tin group 102
Bismuthinite 100
Bismutite 100
Bitter spar 313
Black Band 155
Blowpipe, examination of solids 386
Blue vitriol 105
Bonds, plus and minus 244–245
Borates, green flame by ignition of 253
in analysis 54
reactions of 253
Borax 252
bead, formation of 254

PAGE

Borax, bead, test for **Mn** 189
bead, use of 377
Boric acid 252–254
estimation of 254
formation of 252
occurrence of 252
preparation of 252
properties of 252
solubility of 253
Boron 252
Braunite 177
Bromates, detection of 361
estimation of 362
ignition of 361
preparation of 360
solubilities of 361
Bromic acid 360–362
properties of 360
reactions of 361
Bromides, detection of 359
detection in presence of iodides. 403, 404
estimation of 360
formation of 357
ignition of 359
solubilities of 357
with first group metals 358
Bromine 354–356
detection of 356
estimation of 356
formation of 355
occurrence of 355
preparation of 355
properties of 354
reactions with 355
solubilities of 355
Brookite 205
Brown ring, test for nitric acid 288
Brucine, reactions with nitric acid .. 290
Brucite 220

Cacodyl oxide, test for acetates 258
Cadmium 110–112
detection of 112
estimation of 112
hydroxide 110
notes on analysis of 131
occurrence of 110
oxide 110
preparation of 110
properties of 110
reactions of, comparison with **Bi** and **Cu** 112
salts, absorption by porous substances, separation from **Cu** 112

PAGE

Cadmium salts, fused with K_2S 112
salts, with alkaline tartrates, separation from **Cu** 111
salts, with alkalis 111
salts, with ammonia 111
salts, with barium carbonate 111
salts, with pyrophosphates, separation from **Cu** 111
salts, reactions with $Na_2S_2O_3$, separation from **Cu** 112
salts, reduction of by metals 112
salts, reduction of by ignition 112
separation from **Cu** by H_2S in presence of **KCN** 107
separation from **Cu** by **KCNS** 111
separation from **Cu** by glycerol ... 105
separation from **Cu** by $Na_2S_2O_3$ and Na_2SO_3 112
solubilities of 110
Caesium 239–240
Calamine 183
Calaverite 138
Calcium 216–220
carbonate in spring water 217
carbonate, solubility of 224
detection of 219
detection of by spectrum 219
estimation of 219
group 209
group, directions for analysis of ... 224
hydroxide, formation and properties 217
hydroxide, formation by Na_2S 219
hydroxide, to detect CO_2 218
oxide, formation and properties ... 216
occurrence of 216
peroxide 217
preparation of 216
properties of 216
salts, separation of oxalic from phosphoric acid by 218
salts with Na_2S 219
separation from **Ba** and **Sr** by amyl alcohol 217
separation from **Ba** and **Sr** by $(NH_4)_2SO_4$ 217
solubilities of 217
sulphate, separation from strontium sulphate 215
sulphate, solubility in ammonium sulphate 226
sulphate, to detect strontium 219
Calomel 37
Carbon 254–256
amorphous 255

PAGE

Carbon, detection of 256
dioxide 267–271
dioxide, absorption by $Ca(OH)_2$ ... 269
dioxide, detection in sodium carbonate 270
dioxide, detection by calcium hydroxide 218
dioxide, distinction from H_2S, SO_2, N_2O_3, etc 269
dioxide, formation of 267
dioxide, occurrence of 267
dioxide, properties of 267
monoxide 262–263
preparation of 255
properties of 254
reactions of 255
reduction by ignition with 256
relations of 10
solubilities of 255
Carbonates, acid, decomposition of 236
decomposition of, by acids 270
detection of 270
detection of traces 402
estimation of 271
ignition of 270
occurrence of 267
preparation of 267
reactions with 268
Carbonic oxide, formic anhydride .. 262
Carnallite 228
Cassiterite 82
Cassius' purple 93
Castor & Pollux 239
Celestite 214, 331
Cement 299
Cementite 154
Cerargyrite 46
Cerite 198, 199, 202
Cerium 198
Cerussite 29
Chalcocite 104
Chalcopyrite 45, 104
Chalk 216
Chamber process for sulphuric acid manufacture 331
Chili saltpeter 233, 363, 369
occurrence of 285
Chloric acid 350–353
formation of 350
preparation of 351
properties of 350
separation of, from nitric acid 403
Chlorates, detection of 353
distinction from nitrates 404
estimation of 353

PAGE

Chlorates, formation from chlorine. 340
ignition of. 352
oxidation by ignition of. 352
preparation of. 351
reactions with. 351
solubilities of. 351
Chlorides, detection of. 151
detection of, in presence of bromides. 346, 347, 403
detection of, in presence of cyanides or thiocyanates. 346, 405
formation of. 341–342
ignition of. 345
Chloride of lime, formation of. 348
estimation of, by H_2O_2. 296
Chlorine. 337–341
action on metals. 339
as an oxidizer. 339
detection of. 341
estimation of. 341
formation of. 338
occurrence of. 338
peroxide, formation and properties. 350
properties of. 337
solubilities of. 338
Chlorochromic test for chlorides. 346
anhydride. 151
Chlorous acid, formation and detection. 349
properties of. 349
Chromates. 151, 152
in test for **HCl**. 151
reduction of, by hydrochloric acid. 151
reduction of by H_2S. 150
use in separation of barium. 213
with antimonous salts. 78
with As'''. 151
with ferrous salts. 161
Chrome-ironstone. 148
Chromic acid, detection of. 152
formation of. 151
identification of. 405
Chromite. 148
Chromium. 148–153
distinction from aluminum. 150
estimation of. 152
hydroxide, solubility in ammonium hydroxide. 165
and manganese in third group separation. 166
metal, solubility of. 149
occurrence of. 148
oxidation of. 152

PAGE

Chromium oxides and hydroxides. 148
oxide, solubilities of. 149
preparation of. 148
properties of. 148
reduction of. 152
salts, solubilities of. 149
salts, reaction of. 149
separation from **Al** and **Fe** by H_2O_2. 152
separation from fourth group. 150
separation from **Fe** by $Na_2S_2O_3$ and Na_2SO_3. 146–147
Chromous salts. 149
Cinchonine as a test for bismuth. 102
Citric acid. 258–259
detection of oxalic acid in. 259
distinction from tartaric. 259
properties and reactions. 259
Cinnabar. 37, 313
Clay iron stone. 155
Coal, anthracite. 255
Cobalt. 167–172
bead test. 172
cobalticyanide separation from nickel. 169
detection of. 172
detection of by means of ammonium thiocyanate. 170
detection of in presence of **Ni** by H_2O_2. 190
estimation of. 172
hydroxide. 165
metal, solubilities of. 168
nitrate, effect of ignition with. 377
occurrence of. 167
oxidation of. 173
oxides and hydroxides. 167
phosphate, a distinction from **Ni**. 171
preparation of. 167
properties of. 167
reduction of. 173
salts, solubilities of. 168
salts, with alkalis. 168
salts, with barium carbonate. 169
separation from nickel by ether. 168
separation from nickel by KNO_2. 170
separation from nickel by $KMnO_4$. 172
separation from nickel by NH_4CNS. 172
separation from nickel by nitroso-β-naphthol. 170, 190
Cobaltite. 57, 167
Colloidal sulphides of fourth group. 189
Color, flame tests. 377
Columbite. 198, 203

PAGE

Columbium.....198–199
distinction from **Ti**..... 207
properties and reactions of....198–199
separation from tantalum..... 203
Contact process for sulphuric acid manufacture..... 331
Copper.....104–110
acetoarsenite..... 109
analysis of, notes..... 128
arsenite..... 109
compounds with cyanogen..... 107
detection of..... 109
detection of, in alloys..... 379
detection of traces of, with H_2S... 108
detection of, with **HBr**..... 108
electrical conductors..... 104
estimation of..... 109
ferrocyanide, formation of..... 107
group, metals of.....56, 100
hydroxide of..... 104
occurrence of..... 104
oxides of..... 104
precipitation of, by iron wire..... 110
preparation of..... 104
properties of..... 104
pyrites.....204, 313
reactions of, comparison with **Bi** and **Cd**..... 112
reduction by ignition..... 112
reduction of, by **KCNS**..... 107
salts, detection by potassium xanthate..... 107
salts, reaction with zinc-platinum couple..... 110
salts, reduction of, with H_3PO_2.... 107
salts, separation of, from **Cd** by $Na_4P_2O_7$..... 107
salts, solubilities of..... 105
separation of, from **Bi** by glycerol..... 101
separation of, from **Cd** by glycerol..... 105
separation of, from **Cd** by $Na_2S_2O_3$ and Na_2CO_3..... 112
separation of, from **Cd** by H_2S in presence of **KCN**..... 107
separation from **Cd** by nitroso-β-naphthol..... 107
separation from **Cd** by ammonium benzoate..... 107
separation from **Pd**..... 106
traces, loss of..... 118
traces of, with $K_4Fe(CN)_6$..... 107
Corundum..... 144
Cream of tartar, formation of..... 260

PAGE

Crocoite.....29, 148
Crookesite..... 204
Cryolite.....144, 297
Crythrite..... 57
Cuprammonium salts..... 106
Cupric hydroxide in NH_4OH..... 105
hydroxide, effect of boiling..... 106
hydroxide, formation of..... 106
hydroxide, with glucose..... 106
hydroxide, with tartrates.....105, 106
salts, reaction with glucose..... 105
salts, reaction with iodides..... 108
salts, reaction with $Na_2S_2O_3$..... 108
salts, reduced by SO_2..... 109
sulphide, colloidal..... 108
sulphide, formation of..... 108
sulphide, separation from **Cd** by H_2SO_4..... 108
sulphide, solubility in $(NH_4)_2S_x$.... 108
sulphide, solubility in **KCN**..... 108
sulphide, with K_2S..... 118
sulphide, with $(NH_4)_2S_x$..... 115
Cuprite..... 104
Cuprous iodide..... 108
oxide, formation of, by glucose.... 105
salts, oxidation of, by As_2O_3..... 110
salts, separation, from **Cd** by **S**... 107
salts, with metallic sulphides..... 108
sulphide, formation by $Na_2S_2O_3$... 108
thiocyanate, formation of..... 107
Cyanates, detection of, in presence of cyanides..... 279
Cyanic acid..... 279
Cyanide of silver, distinction from chloride..... 273
Cyanides, detection as thiocyanate.. 275
double, dissociated by acids..... 272
double, not dissociated by acids... 272
estimation of..... 275
guaiacum test..... 275
ignition of..... 274
preparation of..... 272
reactions with..... 272
simple, with mineral acids..... 273
solubility of..... 272
transposition by acids..... 275
Cyanogen properties and reactions..... 271

Danger and Flandin, detection of arsenic..... 69
Daubréelite..... 148
Decomposition of organic material.....374–375

PAGE

Dialysis, separation from organic material by..... 375
Diamond..... 254
Diaspore..... 144
Didymium..... 199
Didymium Earths..... 202
Dimethylaniline, test for nitric acid..... 290
Dimethylglyoxime, test for nickel 176
Diphenylamine, test for nitric acid 290
Dissociation, electrolytic..... 20
Dithionic acid, formation and properties..... 324
Dolomite.....220, 267
Dragendorff's reagent..... 102

Electrolytic dissociation..... 20
Enargite..... 57
Epsom salts.....220, 313, 331
Equations illustrating oxidation and reduction..... 409
rule for balancing..... 246
Erbium..... 200
Ethyl acetate, odor of..... 257
Euxenite.....137, 198, 202, 207
Everett's salt..... 157

Fatty material, removal of..... 375
Feldspar..... 144
Ferric acetate, formation of..... 257
acetate, separation of from chromium..... 157
basic nitrate, separation from aluminum..... 161
and ferrous compounds, distinction..... 165
hydroxide, antidote for arsenic.... 62
phosphate, formation of..... 159
salts, detection of traces..... 158
salts, with acetates..... 157
salts, with $BaCO_3$..... 156
salts, with **HI** and iodides..... 161
salts, with H_3PO_2..... 159
salts, with H_2S..... 150
salts, with **KCNS**..... 158
salts, with $K_3Fe(CN)_6$..... 158
salts, with $K_4Fe(CN)_6$.....157–158
salts, with stannous chloride..... 89
salts, separation from ferrous sulphate..... 156
Ferric thiocyanate, distinction from ferric acetate..... 157
hindrance to reactions of..... 158
Ferricyanides, in distinction between **Co** and **Ni**..... 170

PAGE

Ferricyanides, reactions of..... 278
Ferrite..... 154
Ferrocyanides, detection of..... 277
detection and estimation..... 279
reactions of.....276–277
Ferrotellurite..... 138
Ferrous iron, detection of, in ferric salts..... 158
in the third group..... 164
in the third group with phosphates..... 194
salts, traces in ferric salts..... 158
salts, with chromates..... 161
salts, with HNO_3..... 159
salts, with **KCN**..... 157
Ferrous salts, with $K_3Fe(CN)_6$..... 158
salts, with $K_4Fe(CN)_6$..... 157
sulphate, with gold salts..... 93
First group metals, table of..... 52
Fixed alkalies..... 227
alkali hydroxides on stibine..... 79
alkalis with salts of tin..... 84
Flame, blowpipe, production of..... 376
or color tests..... 385
oxidizing and reducing.....375–376
reactions with copper salts..... 109
Flint..... 299
Fluor-spar.....216, 297
Fluorides, solubilities of..... 298
Fluorine.....297–298
Fluosilicates, formation of.....298–299
Fluosilicic acid.....298–299
in detection of potassium..... 231
in separation of **Ba, Sr** and **Ca**... 213
Formates, formation from cyanides..... 274
Fourth group, directions for analysis..... 189
reagents..... 142
sulphides colloidal..... 189
table of..... 183
Fresenius and **Babo,** detection of arsenic..... 68
Froehde's reagent..... 99
Fulminating gold..... 92

Gadolinite.....202, 207
Galena.....29, 45, 313
Gallium (eka-aluminium)..... 200
Gamma iron..... 154
Garnierite..... 173
Gas-laws..... 21
Gases, absorption of by palladium... 133
Germanium, properties and reactions..... 137

PAGE

Germanium sulphide 118
Glass, etching by hydrofluoric acid. 313
Glauber's salts.....313, 331
Glucinum (Beryllium).....200–201
distinction from yttrium..... 207
separation from aluminum..... 201
separation from cerium..... 198
Glucose, in formation of cuprous oxide..... 105
Gold.....91–93
detection in alloys.....379, 380
detection of..... 93
distinction from **Pd** 133
estimation of..... 93
fulminating..... 92
notes on analysis..... 125
occurrence, properties, etc..... 91
reduction by ferrous sulphate..... 93
reduction with oxalic acid..... 92
salts with alkalis..... 92
salts with stannous chloride..... 89
separation from **Ir** 135
Graphite 254
Greenockite 101, 110
Gypsum.....216, 219, 313, 331

Haematite..... 155
Halogens..... 9
as oxidizers..... 340
compounds, comparative table of 373
hydracids as reducers..... 340
separation of by persulphate method.....347, 403
Hausmannite 177
Heat, upon substances in closed tubes.....376, 382
upon substances in open tubes. 376, 383
Heavy spar 313, 331
Hydriodic acid.....365–368
action on antimonic salts..... 78
action on arsenic salts..... 61
action on ferric salts..... 161
as a reducer.....366, 367
formation of..... 365
Hydrobromic acid.....356–360
detection of **Cu** with..... 108
formation of..... 357
occurrence of..... 357
preparation of..... 357
properties of..... 357
reactions of..... 357
Hydrochloric acid.....341–348
action on Sb_2S_3 77
action on bismuth nitrate..... 102

PAGE

Hydrochloric acid, effect of excess in second group..... 114
formation of..... 341
formation from $MgCl_2$..... 222
gas on arsenic sulphide..... 67
occurrence of..... 341
preparation of..... 342
properties of..... 341
reactions with..... 343
solubilities of..... 342
Hydrocyanic acid.....271–275
formation of..... 272
occurrence of..... 272
on PbO_2..... 274
preparation of..... 272
properties of..... 271
solubilities of..... 272
Hydroferricyanic acid.....277–279
Hydroferrocyanic acid.....275–277
separation from hydroferricyanic acid..... 277
Hydrofluoric acid..... 298
Hydrofluosilicic acid (fluosilicic acid)..... 298
Hydrogen 250, 251
absorption by **Pd** sponge 133
detection of..... 251
estimation of..... 251
formation of..... 250
nascent..... 251
occluded..... 251
occurrence of..... 250
preparation of..... 250
properties of..... 250
reactions with..... 250
reducing action of, with ignition... 251
solubilities of..... 250
peroxide, detection of..... 296
peroxide, estimation of..... 297
peroxide, estimation of bismuth with..... 104
peroxide, formation of..... 295
peroxide, occurrence of..... 295
peroxide, on sulphides of arsenic and antimony..... 121
peroxide, preparation of..... 295
peroxide, properties of..... 294
peroxide, reactions with..... 295
peroxide, reagent to separate **Co** from **Ni**..... 190
peroxide, separation from ozone... 243
peroxide, separation of **Al**, **Fe** and **Cr** with..... 152
peroxide, solubilities of..... 295
peroxide, with arsenic..... 71

PAGE

Hydrosulphuric acid.....315–320
action on copper salts..... 108
action on ferric salts..... 160
dissociation of..... 114
formation of..... 316
gas as a reagent..... 113
gas on antimony..... 67
gas on arsenic..... 67
occurrence of..... 316
on aluminum salts..... 146
on stannic salts..... 86
on stannous salts..... 85
on third and fourth group salts. 142, 164
preparation of..... 316
properties of..... 315
uses as a reagent..... 317
with arsenic acid..... 114
with oxidizing agents..... 114
Hydrosulphurous acid 323, 324
Hydroxylamine, formation and properties..... 286
Hydrozoic acid..... 8, 282
Hypobromous acid, formation and properties..... 360
Hypochlorites, detection of..... 404
formation of..... 348
formation from chlorine..... 344
on arsenic..... 66
Hypochlorous acid..... 348, 349
Hypoiodous acid, existence of..... 363
Hyposulphites, detection of..... 305
ignition of..... 305
Hypophosphites in formation of PH_3..... 305
Hypophosphoric acid..... 307
Hypophosphorous acid 304–306
estimation of..... 306
formation of..... 304
preparation of..... 305
properties of..... 304
reactions of..... 305
solubilities of..... 305
with bismuth salts..... 102
Hyposulphurous acid 323–324

Imperial green..... 109
Indigo test for nitric acid..... 289
Indium..... 201
Ink, common..... 157
sympathetic..... 168
Iodates, detection of..... 371
estimation of..... 371
formation of..... 369
ignition of..... 371

PAGE

Iodates, reactions of..... 370
Iodic acid.....369–371
formation of..... 369
preparation of..... 369
properties of..... 369
reactions of..... 370
Iodide of nitrogen..... 363
Iodides, decomposition by HNO_3... 290
detection as PdI_2..... 133
detection of..... 368
estimation of..... 369
formation of..... 365
ignition of..... 368
occurrence of..... 365
reactions of..... 366
separation of, from bromides and chlorides by $KMnO_4$..... 181
solubilities of..... 365
Iodine.....362–364
detection of..... 364
estimation of..... 364
formation of..... 363
liberation by copper salts..... 108
occurrence of..... 363
on antimonous salts..... 78
on antimony..... 66
on arsenic..... 66
preparation of..... 364
properties of..... 362
reactions of..... 363
separation from **Br** by **Pd**..... 134
solubilities of..... 363
Ions..... 21
Ionization and solution.....20–24
Iridium..... 134, 135
Iron..... 157–162
alpha..... 154
and zinc groups..... 141
beta..... 154
detection of..... 165, 166
detection of traces in copper..... 157
detection of traces..... 157, 158
estimation of..... 162
gamma..... 154
group..... 144
group, separation from **Co, Ni,** and **Mn** by **ZnO**..... 161
hydroxides..... 155
in relation to metals..... 6
occurrence of..... 154
oxidation of..... 162
oxides,..... 154, 155
preparation of..... 154
properties of..... 153
pyrites..... 313

PAGE

Iron, reduction 162
salts, ignition of 161
salts, solubilities of 156
salts, with alkalis 156
salts, with nitroso-β-naphthol 157
salts, separation from **Al** as basic nitrate 161
separation from **Al** and **Cr** by nitroso-β-naphthol 157
separation from **Cr** and **Al** 157
separation from **Ni** by xanthate ... 175
solubilities of 155

Kainite 228
Kieserite 313

Lanthanum 202
Lead 29–36
acetate, properties of 32
chloride 34
chloride, precipitation of 53
chromate, formation of 35
compounds, ignition of 35
detection in alloys 379
detection of 36
estimation of 36
in the test for **Al** 167
iodide, formation and properties 35
notes on analysis of 129
occurrence of 29
oxidation and reduction 36
oxides of 29
oxides, solubilities of 30
preparation of 29
properties of 29
red 29
relation to nitrogen family 7
salts, reactions 32–35
salts, solubilities of 31
solubilities of metallic 30
sulphate, formation and properties of 34
sulphide, formation and properties for 33
tests for 54
Leblanc-soda process 259
Lepidolite 241
Light, action on silver salts 50
Lime, slacked 217
Limestone ($CaCO_3$) 216, 219, 267
Lithium 234–236
Limonite 155

PAGE

Linnaeite 167
Löllingite 57

Magnesia mixture 146
Magnesite 220, 267
Magnesium 220–222
as a reducing agent 222
detection of 222
estimation of 222
hydroxide, formation 220
occurrence of 220
oxalata, separation of, from **K** and **Na** 221
oxide, formation of 220
preparation of 220
properties of 220
removal for detection of sodium ... 242
salts, with ammonium salts 221
salts, with arsenic acid 61
salts, with Na_2S 221
salts, solubilities of 220
Magnetite 155
Malachite 104
Manganates, identification 405
Manganese 177–182
detection of, ... 182, 191
estimation of 182
hydroxides of 177
hydroxides, solubilities of 178
ignition of 182
in third group 164, 166–167, 189
occurrence of 177
oxidation of 182
oxidation to permanganic acid 180
oxides 177
oxides, solubilities of 178
preparation and properties 177
reduction of 182, 183
reduction by sulphites 181
salts, reactions with oxalic acid ... 180
salts, solubilities of 178
salts, with alkalis 179
salts, with sulphides 181
separation from zinc with acetic acid 189
solubilities of 178
with **KI** 181
Manganic acid 177
Magnesite 177
Marble 216, 267
Marcosite 155
Marsh's test 62
Mass action, law of 23, 38
Mayer's reagent 43, 238
Melanconite 104

PAGE

Mercurammonium compounds... 39
Mercuric chloride with stannous chloride... 88
sulphide, formation and properties... 41
sulphide, with K_2S... 118
Mercury... 37–45
chlorides... 42
compounds, ignition of... 43
detection and estimation of... 44
iodides... 42
metallic, analysis of... 379
occurrence of... 37
oxidation of... 45
oxides... 37
preparation and properties of... 37
salts, reactions... 39, 43
salts, solubilities of... 38
solubilities of... 37
sulphide, analysis of... 128
Metals, classification... 10
grouping... 387
table of separation... 388
Metaphosphoric acid... 308
Metastannic acid... 83
Mica... 299
Microcosmic salt... 236
use in ignition... 377
Milk of lime... 217
Millerite... 173
Molybdates in analysis... 54
with phosphates... 98
Molybdenite... 97
Molybdenum... 97–99
deportment in second group... 99
detection of... 99, 124
estimation of... 99
ignition tests... 99
notes on analysis of... 124
occurrence of... 97
oxides and hydroxides... 97
preparation and properties... 97
reduction tests... 99
solubilities of... 97
Molybdic acid... 97
Molybdite... 97
Mottramite... 206
Monazite... 204
Monazite sand... 199

Nascent hydrogen on nitric acid... 286
Neodymium... 199, 203
Nessler's reagent... 43, 237
Niccolite... 57, 173

PAGE

Nickel... 173–176
detection of... 176
detection of, in presence of **Co** by **KI**... 190
distinction from cobalt... 175
estimation of... 176
hydroxides... 173
hydroxides with **KI**... 176
ignition of... 175
occurrence of... 173
oxidation of... 177
oxides... 173
properties and preparation... 173
reduction... 177
salts with alkalis... 174
separation from **Co,** cyanide method... 169–170
separation from **Co,** by nitroso-β-naphthol... 173
separation from **Co,** by KNO_2 170–171
separation from **Co,** by sulphide 175
separation from **Co,** by xanthate... 175
separation from cobalt by NH_4CNS 172
solubilities of... 173
solubility of **NiS** in ammonium sulphide... 175
test for by means of dimethylglyoxime... 176
xanthate, separation from **Fe**... 175
Niobium (Columbium)... 198–199
Nitrates, decomposition by ignition... 288
distinction from chlorates... 404
occurrence of... 285
preparation of... 285
proof of absence... 402
solubilities of... 286
Nitric acid... 285–291
as an oxidizer... 286
Brown ring test... 288
decomposition of, by **HCl**... 287
detection of... 288
detection by diphenylamine... 289
detection by reduction to NH_3.. 286, 289
detection by reduction to nitrite... 289
dissociation by heat... 288
estimation of... 291
formation of... 285
indigo test... 289
in separation of **Sn, Sb** and **As**... 121
sodium salicylate test... 289
test for by dimethylaniline and diphenylamine... 290

PAGE

Nitric acid, with phenol..... 290
with pyrogallol..... 291
with brucine..... 290
occurrence of..... 285
on antimony..... 66
on arsenic..... 66
preparation of..... 285
products of reduction..... 286
properties of..... 285
Nitric anhydride, formation of..... 286
oxide.....104, 221, 283
Nitrites, decomposition by ignition. 284
detection of..... 284
test for nitric acid.....288–290
Nitroferricyanides..... 278
Nitrogen.....281, 282
chloride.....62, 120, 337
combination with elements..... 282
detection and estimation..... 282
family..... 7
formation, occurrence..... 282
peroxide..... 285
properties..... 281
Nitroso-β-naphthol, separation of **Co** and **Ni**.....170, 190
separation of **Cu** from **Cd**..... 107
with iron salts..... 157
Nitroprussides..... 278
Nitrous acid.....284–285
as an oxidizer..... 284
as a reducer..... 284
formation of..... 284
occurrence of..... 284
properties of..... 284
reactions with..... 284
solubilities of..... 284
Noble metals, enumeration..... 7
Nordhausen sulphuric acid..... 332
Notes on detection of acids..... 401
on analysis of calcium group...224–226
on analysis of third group..... 164

Opal..... 299
Orangite..... 204
Order of laboratory study..... 25
Organic substances, removal of..374, 375
Orpiment.....57, 313
Orthoclase..... 144
Osmium..... 133
Osmotic pressure..... 20, 21
Oxalates, decomposition by ignition of..... 402
decomposition by oxidation..... 402
detection of..... 266
distinction from tartrates.....260, 389

PAGE

Oxalates, estimation of..... 266
ignition of..... 266
in 3d, 4th and 5th groups..... 194
reactions of..... 264
solubilities of..... 264
Oxalic acid.....263–266
as a reducer..... 264
decomposition of by H_2SO_4..... 265
formation of..... 263
in separation of gold..... 92
occurrence of..... 263
preparation and properties of..... 263
solubility of..... 264
Oxidation, balancing equations in 244, 245
Oxidizing flame..... 375
Oxygen.....291–293
as a poison..... 292, 293
combinations with ignition..... 293
detection of..... 293
estimation of..... 293
formation of..... 291
occurrence of..... 291
preparation of..... 292
reactions with..... 292
Ozone.....293, 294
separation from H_2O_2..... 295

Palladium.....133, 134
distinction from gold and platinum..... 134
separation from copper..... 106
sponge..... 133
Palladous iodide in analysis..... 133
Paris green.....62, 109
Pearlite..... 154
Pentathionic acid, formation and properties..... 325
Pentlandite..... 173
Perchlorates, preparation and properties..... 353, 354
Perchromic acid..... 153
Periodic acid..... 372
system, table of..... 2
Permanganates identification..... 405
action on antimonous salts..... 78
Permanganic acid..... 178
Persulphate method of separating the halogens.....347, 403
Persulphuric acid..... 336
Petalite..... 241
Phenol reaction for nitric acid..... 290
Phenylhydrazine, on aluminum salts..... 146

PAGE

Phosgene, formation..... 262
Phosphates, changes by ignition... 312
detection.....165, 312, 402
distinction between primary, secondary and tertiary..... 310
estimation of..... 313
in presence of third and fourth group metals..143, 193, 194, 196, 197
occurrence of..... 308
reaction with ammonium molybdate.....193, 311
separation as ferric phosphate..... 193
solubilities of..... 309
Phosphides, formation of..... 312
Phosphine..... 304
Phosphoric acid..... 307–313
preparation of..... 309
properties of..... 307
Phosphoric anhydride, formation of..... 308
Phosphorite..... 216
Phosphorous acid..... 306, 307
detection of..... 307
preparation and properties of..... 306
Phosphorus.....301–304
detection and estimation of..... 304
in combination with the halogens 304
occurrence and preparation of.... 303
properties of.....301, 303
use in match-making..... 302
Phosphotungstates..... 137
Picric acid, in detection of potassium..... 230
Pitch-blende..... 206
Plaster of Paris (calcium sulphate).. 219
Platinized asbestos..... 93
Platinum.....93–97
apparatus, care of..... 95
black..... 93
chloride, as a reagent..... 94
detection of.....96, 124, 379–380
distinction from palladium..... 134
estimation of..... 96
iridium alloys, properties..... 134
notes on the analysis of..... 125
occurrence of..... 94
preparation and properties.....93, 94
reduction of.....95, 96
sponge..... 93
Polarity..... 3
Potassium.....228–232
as a reducing agent..... 232
bichromate, in test for strontium and calcium..... 225
carbonate, as a reagent..... 229

PAGE

Potassium chlorate, in preparation of oxygen..... 292
chloride with platinum chloride... 95
cyanide with copper salts..... 107
cyanide with ferrous salts..... 157
detection of.....229, 232
estimation of..... 232
ferricyanide, formation of..... 277
ferrocyanide, formation of.....273, 276
hydroxide, as a reagent..... 229
iodate, in separation of alkaline earths..... 213
iodide, as a reagent..... 240
iodide, in separation of **AgCl** from $SbCl_3$..... 122
iodide, in the test for nickel..... 190
iodide, on nickelic hydroxide..... 175
iodide, on permanganates..... 181
nitrite in separation of cobalt from nickel.....170, 171
occurrence, preparation and properties of..... 228
picrate..... 230
pyroantimonate.....73, 224
salts, flame test..... 231
thiocyanate with copper salts..... 107
thiocyanate with iron salts..... 158
xanthate, for detection of copper 107
Powder of algaroth..... 75
Praseodymium.....199, 202
Precipitates, formation and removal of.....17, 18
Principles..... 405
Problems in molecular proportions..... 19
in synthesis..... 410
Proustite.....46, 57
Prussian-blue, formation of... 158, 274
Purple of Cassius.....89, 93
Pyrargyrite..... 46
Pyrite.....45, 155
Pyroantimonic acid..... 73
Pyrochlor..... 198
Pyrogallol, as a test for nitric acid..... 291
Pyrolusite..... 177
Pyromorphite..... 29
Pyrophosphoric acid, formation.... 308
Pyrosulphuric acid, formation..... 332
Pyrrhotite.....155, 173

Quartz..... 299

Reagents, care in the addition of... 17
list of..... 415

PAGE

Realgar.....57, 313
Reducing flame, description of..... 375
Reduction, balancing equations in 244, 245
with charcoal.....376, 377, 381
Reinsch's test for arsenic..... 67
Rhodium, distinction from iridium 135
properties and reactions..... 132
Rhodocrosite..... 177
Rochelle salts, composition of..... 260
Rosolic acid as a test for carbon dioxide..... 270
Rubidium, properties and reactions..... 240
Ruby..... 144
Rule for balancing equations..... 246
Ruthenium, properties and reactions..... 129
Rutile..... 205

Salt..... 233
Saltpeter, occurrence..... 285
Samarium, properties and reactions 202
Sand..... 299
Sapphire..... 144
Scandium, properties and reactions.....202–203
Scheele's green and Schweinfurt's green..... 109
Scheelite..... 136
Selenic acid, separation from sulphuric acid..... 140
Selenite..... 216
Selenium, properties and reactions..... 139, 140
Siderite..... 155
Silica (silicon dioxide)..... 300
detection and estimation of..... 301
in the microcosmic bead..... 301
in the third group..... 167
removal of..... 402
solubilities of..... 300
Silicates, decomposition by ignition..... 300
in analysis..... 54
Silicic acid.....299–301
Silicon..... 299
distinction from tantalum..... 203
Silico-fluoride (fluosilicate)..... 298
Silicon fluoride, formation.....297, 298
preparation and properties..... 298
separation from thorium..... 205
Silver.....45–50
arsenate and arsenite, formation.. 62
bromate, properties of..... 361

PAGE

Silver chloride, formation and properties..... 48
cyanate in distinction from cyanides..... 279
detection of.....50, 380
estimation of..... 50
in presence of mercury salts..... 55
iodate, properties of..... 370
mirror, formation by tartrates.... 261
nitrate, action on stibine..... 79
nitrate with stannous and antimonous salts.....78, 79, 88
occurrence and properties of..... 45
salts, action of light upon..... 50
solubilities of..... 46
thiocyanate, separation from silver chloride..... 281
Sipylite..... 207
Skutterudite..... 167
Smaltite.....57, 167
Soapstone..... 299
Soda lime on stibine..... 79
process, Le Blanc's..... 267
process, Solvay's..... 268
Sodium.....232–235
amalgam, action with arsenic..... 64
as a reducing agent..... 235
detection of.....73, 234
estimation of..... 235
flame test..... 234
hydroxide, formation of..... 233
nitroferricyanide as reagent... 236, 320
occurrence of..... 233
phosphate as reagent..... 233
Sodium phosphomolybdate as reagent.....98, 238
preparation and properties of..232, 233
pyroantimonate.....73, 80
pyrophosphate with copper and cadmium..... 107
salicylate test for nitric acid..... 289
sulphide, preparation of..... 317
thiosulphate on cupric salts..... 108
thiosulphate with antimony salts.. 78
thiosulphate with third group metals.....146, 147
Solids, conversion into liquids..... 328
decomposition upon ignition...382, 383
effect on ignition with cobalt nitrate..... 384
preliminary examination of..... 375
separation of..... 17
table for preliminary examination..... 382
Solubility, degrees of.....15, 16

PAGE

Solubility-product 24
Solution and ionization 20–24
Solvay soda process 268
Sonnenschein's reagent 98
Sperrylite 94
Stannic salts, solubilities 84
sulphide, formation and properties of 86
Stannite 82
alkali, as a test for bismuth 103
Stannous chloride on mercury salts 43
chloride as a reducing agent 88
chloride with gold salts 93
chloride with molybdic acid 99
salts, distinction from stannic salts 125
salts, solubilities 84
salts with silver nitrate 87
salts with sulphurous acid 86
sulphide, formation and properties 85
Stephanite 46
Stibine, decomposition by soda lime 79
formation of 79
reaction with fixed alkali hydroxides 79
reaction with silver nitrate 79
separation from arsine 65
Stibnite 72
Strontianite 214
Strontium 214–216
detection of 216, 219
estimation of 216
hydroxide, formation 214
occurrence of 214
preparation and properties of 214
sulphate, distinction from $CaSO_4$ 215
sulphate, separation from $BaSO_4$ 215
Sulphates, detection of 335
estimation of 336
ignition of 335
preparation of 332
reduction by ignition with carbon 256
solubilities of 333
Sulphites, detection of 330
distinction from sulphates 330
estimation of 330
ignition of 330
interference in test for oxalates ... 402
preparation of 327
separation from sulphates by **Ba** salts 213
solubilities of 328

PAGE

Sulphides, detection 320
estimation of 321
formation of 316
ignition of 319
reactions of 318, 319
solubilities of 28, 317
Sulphur 313, 315
combinations on ignition of 315
detection and estimation of 315
formation of 313
in the tin group 118
occurrence of 313
oxidation by reagents 314, 315
oxides 313
precipitation of 54, 114, 115
preparation and properties of .. 313, 314
reactions in forming sulphides 314
relations of 9
separating copper from cadmium 107
solubilities of 314
Sulphuric acid 331–336
detection in presence of sulphates 335
formation and occurrence of 331
manufacture of 331
properties of 331
reactions with 333–335
separation from **Se** 140
separation from **Te** 139
anhydride, preparation of 331
Sulphurous acid 327–330
on arsenic acid 60
and sulphites as reducers 329
occurrence of 327
preparation and properties of 327
formation of 327
reduction of cupric salts 108
solubilities of 328
on stannous salts 86
Sylvanite 138
Synthesis, problems in 410

Table for acids as precipitated by barium and calcium chlorides ... 398
for acids precipitated by silver nitrate 399
for acids, preliminary 390
for analysis in presence of phosphates by the use of alkali acetates and ferric chloride 196
for analysis in presence of phosphates by use of ferric chloride and barium carbonate 197
for analysis of the Silver Group (first) 52

PAGE

Table for analysis of the Copper Group (second) 126
for analysis of the Tin Group (second) 116
for analysis of the Iron Group (third) 163
for analysis of the Zinc Group (fourth) 188
for analysis of the Calcium Group (fifth) 223
of grouping of the metals 387
of separations of the metals 388
of separation of the ammonium sulphide precipitates of the Iron and Zinc Groups 192
of solubilities 411
Tannic acid with iron salts 157
Tantalite 198, 203
Tantalum, distinction from silica .. 203
distinction from titanium 203
properties and reactions of 203
separation from columbium 203
Tartar emetic, composition of 260
Tartaric acid 259–261
in detection of potassium 229
distinction from citric acid 259
formation and properties 259–260
Tartrate calcium, deportment with water 260
detection of 260
distinction from citrates 260
distinction from oxalates 260, 401
estimation of 261
Tartrates, ignition 261
reactions 260
solubilities 260
Tellurite 138
Tellurium 138–139
distinction from selenium 139, 140
properties and reactions of 138, 139
separation from sulphuric acid 139
Tenorite 104
Terbia 203
Terbium 203–204
Tetradynite 138
Tetrathionic acid, formation and properties 325
Thallious iodide 204
Thallium, properties and reactions. 204
Thioacetate in formation of sulphides 316
Thiocyanates, reactions with 280
test for cobalt by means of 170
Thiocyanic acid as a reducer 281
properties of 280

PAGE

Thionic acids, table of comparisons 326
Thiosulphates, detection of 323
distinction from sulphates and sulphites 323
estimation of 323
ignition of 323
formation and properties of 321
Thiosulphuric acid 321–323
Third group reagents 142
Thorite 204
Thorium 204–205
Tin 82–89
creaking of 82
detection of 88, 122, 379
estimation of 88
Group, metals of 56
Group, separation from Copper Group 115
Group, sulphides with $(NH_4)_2S_x$ ... 115
occurrence of 82
oxidation of 88
oxides and hydroxides 82
preparation and properties of 82
notes on the analysis of 124, 125
relation to Nitrogen Family 7
reduction by ignition 87
salts with the alkalis 84
salts with hydrosulphuric acid 85
separation from antimony 81
separation from antimony sulphides 123
separation from arsenic 118
solubilities of 83
sulphides, colloidal 115
with antimony and with arsenic .. 87
Tinstone 82
Titaniferous iron 205
Titanite 205
Titanium 205–206
distinction from columbium 206
distinction from tantalum 203
properties and reactions of 205
separation from thorium 205
Triphylite 241
Trithionic acid, formation and properties 324
Tungsten, properties and reactions 136, 137
Turnbull's blue 155

Unit of quantity 23
Uranium, properties and reactions. 206
Urea, from ammonium cyanate 279

PAGE

Valence, negative 3
Valentinite 72
Vanadinite 206
Vanadium 206, 207
Volatile alkali (ammonium hydroxide) 221
Volborthite 206

Wad 167
Water, action on bismuth salts 101
action on antimonous salts 75
Welsbach burners 209
Witherite 211
Wolframium (tungsten) 136
Wulfenite 97

Ytterbium properties and reactions 207
Yttrium 207

PAGE

Zincates, formation of 184
Zinc 183–186
blende 183, 313
blende (Freiburg) 201
detection and estimation of 186
Family 5
granulated 63, 183
Group, table for analysis 188
Group, comparative reactions 187
hydroxide and oxide 184
ignition of 186
occurrence of 183
oxidation of 186
platinized 183, 250
preparation and properties 183
reduction of 186
salts, solubilities and reactions of 184
sulphide, formation in presence of acetic acid 184
Zircon 209
Zirconium 209

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